

ABSTRACT

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ZEOLITE CHARACTERISTICS FOR MAXIMUM URANIUM UPTAKE FROM SOLUTION AND POTENTIAL FOR URANIUM IMMOBILIZATION IN SOILS

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Zeolites, having stable porous structures and high ion exchange capabilities are potential buffer materials that can be added to a soil matrix to improve the ion exchange ability. This study investigated the performance of various zeolites for the uptake of uranium as soluble UO_2^{2+} , with the ultimate goal being to develop an *in situ* ion trap to immobilize potentially leachable residue in uranium contaminated soils. The natural zeolite, clinoptilolite and synthetic zeolites, K-L, LZY, 13X, and mordenite were evaluated for the uptake of UO_2^{2+} in both batch and column percolation studies. In the preliminary batch and column studies, mordenite, LZY, and K-L were most effective for uranium uptake. The pH was an important factor in governing which uranium species would be present in solution. In the pH controlled batch studies, mordenite demonstrated superior performance to the other zeolites as well as to a clay-soil for uranium uptake. With time, initially adsorbed uranium was dissolved from the soil into solution whereas the zeolite showed no such release of uranium. Uranium uptake was found to be dependent on zeolite pore size, solution pH, cation concentrations, and amount of sorbent.

ZEOLITE CHARACTERISTICS FOR MAXIMUM URANIUM UPTAKE FROM
SOLUTION AND POTENTIAL FOR URANIUM IMMOBILIZATION IN SOILS

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LIST OF ABBREVIATIONS

BUFF	Buffered solution
CLINO	Zeolite Clinoptilolite
DOE	U. S. Department of Energy
FEMP	Fernald Environmental Management Project
FERMCO	Fernald Environmental Remediation Management Company
FT-IR	Fourier Transform - Infrared Spectroscopy
ICP-MS	Inductively coupled argon plasma-mass spectrometry
h	Hour(s)
K-L	Zeolite L-potassium form
LZY	Zeolite Y
MORD	Zeolite Mordenite
U	Uranium
UA	Uranyl Acetate
UN	Unbuffered solution
X	Zeolite 13X
XRD	X-Ray Diffraction Spectrometry

CHAPTER 1

INTRODUCTION AND STATEMENT OF THE PROBLEM

1.1 Background

The operation of uranium production facilities during the past four decades have resulted in soils contaminated with this radionuclide from many sources. These sources include: deposition of airborne uranium particulates from facility stacks, leaks/spills of uranium-rich solvents, and process effluents from aqueous and non-aqueous extraction/treatment processes. It is estimated that there are over 2,000,000 m³ of soils that are contaminated with uranium.¹ Chemical soil washing techniques have been demonstrated to be an effective strategy for the removal of large concentrations of radioactive wastes from these soils.¹ This approach provides a restoration of the soils to fertile lands as well as avoids the costly disposal of these soils in conventional low-level radwaste burial sites. This technique, using sodium or ammonium carbonate/bicarbonate, was demonstrated to be capable of reducing the concentration of uranium at the Fernald Environmental Management Project (FEMP) site in Fernald, Ohio from approximately 500 to 50 ppm (mg/Kg) in a best case.² Following this procedure, the residual amounts of radioactive metal are still a serious environmental concern. The major concerns include: 1) migration of the metal into aquifers, 2) migration of the metal into plant tissues and ultimately into the food chain, and 3) the deterioration of soil physicochemical properties that result from soil washing procedures.

1.2 Zeolite Usage In Nuclear Waste Treatment

Since the 1980's, zeolites have been playing a major role as selective ion exchangers. Zeolites were used in the 1979 Three Mile island accident, NPP, USA, for the uptake of ^{127}Cs and ^{90}Sr and at the Site Ion Exchange Plant (SIXEP) at British Nuclear Fuels site at Sellafield.^{3,4} On a laboratory scale, studies have shown numerous other zeolites, such as chabazite and mordenite, to be equally as effective in the cleanup of low- and medium-level active waste.⁵ There is less work on the application of zeolites in the uptake of actinides. Mimura et. al. investigated the uptake of americium (Am^{3+}) on a wide range of zeolites including A, X, Y, L, chabazite, mordenite, phillipsite, erionite and clinoptilolite. Mordenite and L were found to be the most effective.⁶ Amini and Dyer reported similar results for zeolite L while Brezhneva et. al. have found that zeolite NaY is effective in the uptake of uranyl ions.^{7,8} Andreeva and Chernyavaskaya also reported that high-silica zeolites, mordenite and clinoptilolite can effectively ion exchange uranyl.⁹ Dyer and Josefowicz investigated a wide range of natural and synthetic zeolites for thorium uptake and reported that clinoptilolite and mordenite-rich types were good sorbents.¹⁰ Qadeer et. al. later reported that zeolite 13X was very effective in the sorption of Thorium as well as for uranyl at a pH of 3.0.¹¹ In all cases, the percentage of adsorption was found to be heavily dependent on the pH of the solution at which the experiment was performed. In terms of the pH dependency, low solution pH (1.0 - 3.0) facilitates ion exchange processes while higher pH results in the adsorption/precipitation of hydrolyzed uranium species on the zeolite surfaces.

As the Si/Al ratios of zeolites are known to affect their stability, exchange capacity and selectivity, several of the above mentioned zeolites were examined for these properties.

1.3 Statement Of The Problem

Experimental studies and speciation modeling done to characterize the nature of uranium at two contaminated sites, Fernald, Ohio and Oak Ridge, Tennessee, found that the metal exists primarily (80-90%) in the hexavalent oxidation state.^{1,2} Results of these experiments also show that for uranium-containing waste solutions at a pH of 7, over 80% of the uranium exist predominantly as anionic carbonate complexes, specifically bis-carbonate $\text{UO}_2(\text{CO}_3)_2^{2-}$ and tris-carbonate $\text{UO}_2(\text{CO}_3)_3^{4-}$.¹ For very dilute uranium solutions (<238 ppm), the metal exists primarily as UO_2^{2+} at pH less than 5.9.¹² In acid rain situations where the soil pH can be lowered to <6, the uranium will exist primarily as the cationic species, UO_2^{2+} . The hexavalent uranium species are quite soluble and are therefore capable of subsurface migration. The rates of solubilization of uranium from the soils are dependent upon factors such as amount of rainfall, rainfall pH, soil physicochemical properties and soil pH.² Therefore, pH plays a major role in the solubilization as well as the remediation of uranium from soils. The ability of the zeolite to effectively remove uranium from solution is a precursor to the development of an *in situ* ion trap for the immobilization of uranium in soil.

1.4 Objective

The primary objective of this research was to investigate the potential of zeolites to restrict movement of uranium in contaminated soils and leachates from these soils.

CHAPTER 2

SURVEY OF RELEVANT LITERATURE

2.1 Uranium Contamination to the Environment

Heavy metals in soils have received great interest and attention due to the greater understanding of their toxicological importance in ecosystems, agriculture and human health. The growing scientific and public health awareness of environmental issues has brought about the need for more analytical techniques to measure contaminant concentrations. Moreover, the primary concern is for accurate measurements of these contaminants and an appropriate method of their removal.

Uranium mill tailings are the residue, usually in the form of a fine sand, that are left after the mining and extraction of uranium from ores. Tailings are produced in very large volumes and contain low levels of naturally occurring radioactive materials.¹³ Natural radioactive atoms in the earth—primarily uranium, thorium, radium, and radon, expose humans to varying amounts of radiation at all times. Of the total amount of radiation that the average person in the United States receives every year, only 82 percent comes from natural sources.¹³ Other exposure to radioactive sources comes from such sources as medical diagnosis, medical therapy, and nuclear weapons production and testing sites. These radioactive particles (from nuclear sources) can cause damage to many living organisms. Uranium-238 is the chief constituent of natural uranium and has a half-life of 4.468×10^9 years.¹⁴ This stability is cause for great concern in exposure from radioactive uranium to the environment. Radioactive material can reach the environment and people through direct contact or by the movement of radionuclides through the air, soil, surface

water, or groundwater. These basic pathways of exposure from any given production facility or contaminated site depends heavily on three important factors: 1) type of hazardous waste or radioactive material, 2) the geology of the area, and 3) the environment or climate of the area.

2.2 Uranium in Solution

Uranium has four valency states, of which the tetravalent (4+) and hexavalent (6+) states are readily accessible in solution.¹⁵ The uranium species that are present in solutions, and especially dilute solutions, is heavily dependent upon the pH of the solution. Table 1 summarizes the work of Palei, who found that above solution pH of 5.90, the uranyl hydroxides begin to precipitate.

Table 1. Effective pH of solution for the beginning of hydroxide precipitation as a function of the UO_2^{2+} concentration in solution.

Concentration of Uranium species in solution, M	0.1	0.01	0.001	0.0001	0.0003	0.00001
pH of Solution at beginning of Hydroxide Precipitation	4.47	5.27	5.90	6.62	6.80	7.22

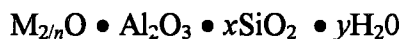
For dilute solutions with a uranium concentration of 0.001M below pH 5.90, the uranium in solution exists primarily as UO_2^{2+} .¹² This uranyl ion is very soluble in aqueous environments and would be easily leached from the soil at or below the pH of acid rain. The 6+ oxidation state is the most stable and forms soluble uranyl complex ions (UO_2^{2+}) which play the most important role in uranium transport during weathering.¹⁴

2.3 Zeolites

Zeolites are molecular sieves that have stable microporous structures and high ion exchange capacities and are potential buffer materials that can be added to a soil matrix to improve the ion exchange ability of the soil. As a class of molecular sieves, zeolites are classified by having a aluminosilicate framework and only the aluminosilicate molecular sieves can be termed as zeolites.¹⁶ As all molecular sieves have the ability to separate components of a mixture on the basis of size and shape, zeolites have an anionic charge framework that allows the exchange of cations within their framework. They have the capacity to exchange up to 2.2 mmol cations per gram of zeolite.¹⁶

2.3.1 Zeolite Framework

Zeolites have an extensive three-dimensional network of oxygen atoms and situated within these tetrahedral sites formed by the oxygen atoms can be an Al^{3+} or a Si^{4+} . The framework charge is determined by the AlO_2^- tetrahedra in the structure. Various cations can occupy the nonframework positions and balance this charge. The empirical formula for a zeolite is usually written as:



M represents the exchangeable cations, usually from group I or group II ions, n represents the valence of the cation, x is equal to or greater than 2, and y is the number of water molecules.¹⁶ Within the crystalline framework structure there are voids and channels of discrete size in the range of 3 Å to 8 Å, depending on the structure. The water molecules of the zeolite are found in these cavities and channels, as are the cations that neutralize the

negative charge created by the presence of the AlO_2^- tetrahedra in the structure.¹⁶ These cations typically include: the alkaline and alkaline earth cations, NH_4^+ , H_3O^+ (H^+), TMA^+ (tetramethylammonium), and other nitrogen-containing organic cations, and the rare earth and noble metal ions.¹⁶

2.3.2 Zeolite Classifications and Pore Size

Zeolites can be classified by pore size as well as dimensionality and shape. The first level of the classifications of zeolite is pore size and for most zeolite applications, this simplest classification is adequate.¹⁶ The pore opening for each zeolite is determined by the number of T atoms, where T atoms are the Si or Al, that define the pore opening. There are only three pore openings classifications known to date in the aluminosilicate zeolite system that are of interest in adsorbent or catalytic applications.¹⁶ These are small (8-member ring), medium (10-member ring), and large (12-member ring) pore zeolites.

Factors that influence the size and shape of the zeolite pore opening are:

1. Configuration of the T and O atoms relative to each other
2. Si/Al ratio
3. Size of cation
4. Location of cation
5. Temperature

Although structure dictates the shape of the pore opening, this opening is also affected by the spatial requirement for the cation and the number of cations present in the channels and cavities. In essence, a divalent cation implies that fewer ions will be used to balance the framework charge and thus the opening dictated by structure alone will be relatively observed whereas a monovalent cation requires twice as many ions and the spatial requirements thereof may reduce or contract the effective pore opening.

observed whereas a monovalent cation requires twice as many ions and the spatial requirements thereof may reduce or contract the effective pore opening.

2.4 Soil Chemistry

Soils are very complex systems that are formed by the weathering of parent rocks as a result of the interactive geological, hydrological, and biological processes.¹⁷ Soils are porous in nature and are vertically stratified in different levels or horizons.¹⁸ Soils undergo continual exchange of matter and energy with the atmosphere (air), hydrosphere (water), and biosphere (land).¹⁷ Chemical species are transported to and from soil particles by the soil solution. Soil solution is the aqueous portion of soil that contains the dissolved matter from soil chemical and biochemical processes as well as matter exchanged with the hydrosphere and biosphere.¹⁹

The majority of dissolved mineral matter in soil is largely present as ions. Prominent among these cations are H^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and low levels of Fe^{2+} , Mn^{2+} , and Al^{3+} .¹⁷ One of the most important functions of the soil is the exchange of cations. The ability of a soil to exchange cations is the cation exchange capacity. The cation exchange capacity (CEC) is defined as the number of milliequivalents (meq) of monovalent cations that can be exchanged per 100 g soil (dry-weight).²⁰

All nutrients are made available to the plants by the soil and soil solution. When metal ions are taken up by plant roots, hydrogen ion is exchanged for these metal ions and this along with metal ion leaching by carbonic acid tends to make the soil acidic.¹⁷ Soils have a buffering capacity and can resist the changes in pH. This buffering capacity is dependent on the composition of soil.

CHAPTER 3

MATERIALS AND METHODS

3.1 Approach

Characterization studies performed on FERMCO soils show that they may contain up to 500 mgU/Kg soil, predominantly hexavalent uranium existing as UO_2^{2+} , which is more soluble than the tetravalent species.²² There exists a wide variation in the speciation of hexavalent uranium from one site to another and in most cases, with the depth at a given site, the uranium existing mainly as $\text{UO}_2(\text{CO}_3)_2^{2-}$. The predominantly dissolved species are predicted to be anionic, because this provides a ready explanation for the apparent lack of incorporation into clays (which are predominantly cation exchangers) and the apparent enhanced mobility at the site.²² In this study, the performance of various zeolites for the uptake of soluble UO_2^{2+} was investigated with the ultimate goal being to develop an in situ ion trap to immobilize potentially leachable residue in contaminated soils. The approach was broken down into three major objectives: 1) screen several zeolites for the uptake of uranium from solution, 2) determine the optimal conditions for the uptake of uranium from solution; mainly solution pH, cation (uranium) concentration, and amount of sorbent per volume of solution, and 3) determine the optimum conditions for the uptake of uranium from solution in the presence of soil.

3.2 Materials and Equipment

Uranyl acetate salt ($\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and a 1000 ppm uranium reference standard were obtained from Electron Microscopy Sciences and Fisher Scientific, respectively. Equipment and apparatus used included, Perkin Elmer Elan 5000 Inductively

Coupled Argon Plasma/Mass Spectrometer (ICP/MS), Orion 420A pH meter and electrode, rotary agitator (18 rpm maximum frequency), with capacity for twelve 20 ml vials, centrifuge (IEC-HN-S11), Oxford micropipettors, analytical balance with $\pm 0.0001\text{g}$ capability, 20 ml polyethylene vials, 50 ml burets, glass wool, and assorted laboratory glassware. See Appendix A, page 57, for a complete list of all equipment, supplies, and instrument parameters.

3.3 Chemical Analysis of Soil

A uranium free soil was obtained from an area approximately 2 km from the FEMP site for a comparative study. Based upon the appearance of the soil, it was concluded that this particular soil had a medium-high clay content. Soil and clays are capable of ion exchange and the basic nature and properties of the soil were also studied.

3.3.1 Determination of Soil pH

Three 5.000g samples of soil were mixed with 5.00ml of double deionized water and allowed to equilibrate for 1, 8, and 24 hour intervals each. The pH of the soil was measured on an Orion 420A pH meter.

3.3.2 Determination of Cation Concentration in Soil

The soil was tested under buffered and unbuffered conditions with solutions of pH 3.00, 4.00 and 5.5 for major nutrient metal cations normally present in soil. Batch studies were performed using 0.1000g soil in 20.0 ml of solution. The batch studies were conducted in 20 ml polyethylene vials and placed on a tube rotator at 18 rpm for varying time periods depending upon the length of the study. The samples were removed from the

rotator and centrifuged at 2500 rpm for 10 minutes. The supernatant was then transferred to a clean polyethylene vial and acidified with 0.2 ml concentrated nitric acid, ACS plus grade, to preserve the metal ions in solution for ICP-MS analysis. Samples were serially diluted to the ppb range in 10.0 ml volumetric flasks using a 1% HNO₃ solution. The different metal cation concentrations were determined by ICP/MS on a standard calibration curve from 0 to 500 ppb.

3.3.3 Determination of Soil Exchangeable Cations

The cation exchange capacity of the soil was determined by the ammonium-saturation method (See Appendix B, page 59 for standard method protocol). The milliequivalents of ammonium exchanged were determined by titration with standard 0.1N H₂SO₄ after displacement and distillation. (See Appendix B, page 60 for method).

3.4 Zeolite Preparation

The zeolites used in this study were both natural and synthetic. Five zeolites were screened for their adsorption of uranium from solution as candidates for the soil remediation study. Mordenite, clinoptilolite, K-L were ground with a mortar and pestle then sieved to a 80 - 120 mesh. Zeolite X and Y were received as powders containing no binders and sieved to a 80-120 mesh. The sieve system contained four sieve chambers, specifically 35-45, 45-60, 60-80, and 80-120 screens. The screen sizes are in particles per linear spacing units.

The sources of zeolites used in this study are listed in Table 2. Their phase purities were characterized by X-ray diffraction. Diffraction patterns were recorded on a Phillips

Table 2. List of zeolites used in sorption studies.

Zeolite	Description	Zeolite Pore Dimensions (Å)	Source
Mordenite	synthetic, powder and extrudates	6.5 x 7.0	Union Carbide, USA
Zeolite 13 X	synthetic, powder and extrudates	7.4	Union Carbide, USA
Zeolite LZY	synthetic, powder and extrudates	7.4	Union Carbide, USA
Zeolite K-L	synthetic, powder	7.1 x 7.1	Chemie Uetikon, Switzerland
Clinoptilolite	natural, powder and extrudates	7.6 x 3.0	Ash Meadows, USA

X'PERT Diffractometer equipped with $\text{CuK}_{\alpha 1}$ radiation. The instrument settings were as follows: voltage, 40mV; current, 40mA; slit widths, 0.2nm; and scans were recorded between 5 to 50 degrees 2θ for 1 hour.

3.4.1 Preparation of Ca-Exchanged Mordenite

The zeolite selected for this study was cation exchanged with a Group II cation, Ca^{2+} , to test the effect of the larger species on the adsorption of uranium from solution. An exchange system was set with 50.0 ml of 1.00 M $\text{Ca}(\text{NO}_3)_2$ per 1.000 g zeolite (See appendix B, page 61, Ca-Exchanged form of Mordenite). The phase purity was

characterized by X-ray diffraction recorded at scans between 5 to 50 degrees 2θ for 1 hour.

3.5 Adsorption Designs

Adsorption is the process that describes the interaction between a molecule and a surface.²³ Two adsorption designs were used: (1) column percolation studies using 0.1000 g of zeolite and solutions of three concentrations of uranium in solution and (2) batch studies using 0.1000 g zeolite in 20.0 ml of solutions of three concentrations of uranium in solution in which a tube rotator (18 rpm) was used for mixing. These adsorption designs were also studied using the FEMP-like soil (1.90 g) mixed with 0.1000 g zeolite and the impregnated soil (1.90 g) mixed with 0.1000 g zeolite with double distilled water as the effluent.

3.5.1 Soil Loading of Uranium

The uranium free soil was dried in an oven at 60 °C for a period of 4 hours. Two 250.0g portions of this dry soil was then impregnated with 250 ml of solutions of uranyl acetate in 50 and 500 ppm U concentrations. The solution was allowed to be absorbed by the soil for 1 hour at room temperature then placed in a 60°C oven for 24 hours.

3.5.2 Column Percolation Studies

Column studies were conducted in 50.0 ml burets, with dimensions of 80 cm x 23 mm dimensions. Columns were packed with glass wool, followed by sand (dried in an oven at 60 °C for 1 hour), and a layer of zeolite or zeolite mixed with soil. Initial tests were performed with solutions of uranyl acetate passing through the column packed with

glass wool, sand and 0.1000g zeolite to determine the uptake of uranium for each zeolite. Subsequent tests were performed with 0.1000g zeolite mixed with 1.900 g of the uranium loaded soil (50 and 500 ppm U) and double deionized water as the leachate. The soil was also tested in a packed column for leaching of the uranium from the soil using a solution of 1% HNO_3 and double deionized water. The samples were collected in 20.0 ml aliquots in polyethylene vials and centrifuged at 2500 rpm for 10 minutes. The supernatant was then transferred to a clean polyethylene vial and acidified with 0.2 ml concentrated nitric acid, ACS plus grade, to maintain the uranium in solution for ICP-MS analysis. Samples were diluted to the ppb range in 10.0 ml volumetric flasks using a 1% HNO_3 solution.

3.5.3 Batch Studies

Batch studies were performed using 0.1000g zeolite and 0.1000g soil in 20.0 ml of solution containing three different concentrations of uranium; 23.8, 119, and 238 ppm. The batch studies were conducted in 20 ml polyethylene vials placed on a tube rotator at 18 rpm for varying time periods depending upon the length of the study. The samples were removed from the rotator and centrifuged at 2500 rpm for 10 minutes. For ICP-MS analysis, the samples were prepared as listed in section 3.5.2.

3.5.4 pH Controlled Batch Studies

Buffered and unbuffered solutions were used at specific pH's and at two concentrations of uranium, 23.8 and 238 ppm. The acetic acid/acetate buffered stock solution was prepared to 0.01M concentration of sodium acetate and acetic acid. The citric acid/citrate buffered stock solution was also prepared to a 0.01M concentration of

sodium citrate and citric acid. The unbuffered stock solutions were prepared using concentrated nitric acid, ACS plus grade, to adjust the pH to the specified level. The uranyl acetate was then added to the solution and the pH was readjusted for both the buffered and unbuffered solutions similarly. Batch studies were performed using 0.1000 g zeolite and 0.1000 g soil in 20.0 ml of solution containing two different concentrations of uranium, 23.8 and 238 ppm. The pH batch studies were conducted in 20 ml polyethylene vials and placed on a tube rotator at 18 rpm for varying time periods depending upon the length of the study. The samples were removed from the rotator and centrifuged at 2500 rpm for 10 minutes. For ICP-MS analysis, the samples were prepared as listed in section 3.5.2.

3.5.5 Mordenite vs. Soil Competitive Adsorption

The influence of the soil on the adsorption ability of mordenite was determined. Buffered and unbuffered solutions were prepared as listed in 3.5.4. The uranium concentration was 238 ppm. Batch studies were performed using 0.1000 g mordenite, 0.1000 g soil, and 0.1000 g mordenite mixed with 0.1000 g soil in 20.0 ml of solution containing 238 ppm uranium following the procedure listed in 3.5.4 for sample batching and prepared for ICP/MS analysis as listed in 3.5.2.

3.5.6 The Effect of Solution/Mordenite Ratio on Uranium Uptake

The optimum amount of zeolite required to reach equilibrium with uranium adsorption was investigated. Buffered and unbuffered solutions were prepared as listed in 3.5.4. The uranium concentration was 238 ppm. Batch studies were performed using

0.1000, 0.2000, 0.4000, 0.6000, 0.8000, and 1.000 g of mordenite in 20.0 ml of solution containing 238 ppm uranium. The pH batch studies were conducted following the procedure listed in 3.5.4 for sample batching and prepared for ICP/MS analysis as listed in 3.5.2.

3.5.7 Uranium Adsorption in the Presence of Competing Cations on Mordenite

The effect of competing cations, namely potassium, calcium, and magnesium, on the adsorption of uranium from solution by mordenite was investigated. Buffered and unbuffered solutions were prepared as listed in 3.5.4. Binary cation batch studies were conducted with potassium (391 and 3910 ppm), calcium (400.8 and 4008 ppm), and magnesium (243 and 2430 ppm) in pH solution with 238 ppm uranium. The pH batch studies were conducted following the procedure listed in 3.5.3 and prepared for ICP/MS analysis as listed in 3.5.2.

3.6 Desorption Designs

The purpose of this experiment was to investigate the leaching characteristics of uranium loaded mordenite. Samples previously adsorbed with uranium were tested for leachability of uranium as a function of time and/or pH.

3.6.1 Uranium Desorption from Soil

The soil samples used in this study were previously subjected to eight hours of mixing with the buffered and unbuffered solutions containing 23.8 and 238 ppm uranium. The soil samples were tested for leachability of uranium using solutions of the same pH as that of the adsorption study. The soil desorption studies were conducted in 20 ml

polyethylene vials and placed on a tube rotator at 18 rpm for 72 hours. The samples were removed from the rotator and centrifuged at 3000 rpm for 15 minutes. For ICP-MS analysis, the samples were prepared as listed in section 3.5.2.

3.6.2 Soil Desorption - Mordenite Adsorption

The soil samples used in this study were previously subjected to eight hours of mixing with the buffered and unbuffered solutions containing 23.8 and 238 ppm uranium. The soil samples were tested for leachability of uranium using solutions of the same pH as that of the adsorption study. The soil desorption-mordenite adsorption studies were conducted in 20 ml polyethylene vials containing an original 0.1000g sample of soil (desorption) and an additional 0.1000g portion of mordenite (adsorption). These samples were placed on a tube rotator at 18 rpm for 72 hours. The samples were removed from the rotator and centrifuged at 3000 rpm for 15 minutes. For ICP-MS analysis, the samples were prepared as listed in section 3.5.2.

3.6.3 Uranium Desorption from Mordenite

The mordenite samples used in this study were previously subjected to 24 and 72 hours of mixing with the buffered and unbuffered solutions containing 23.8 and 238 ppm uranium. The mordenite samples were tested for leachability of uranium using double deionized water. The mordenite desorption studies were conducted in 20 ml polyethylene vials and placed on a tube rotator at 18 rpm for 24 and 72 hours, respective to the adsorption study. The samples were removed from the rotator and centrifuged at 3000

rpm for 15 minutes. For ICP-MS analysis, the samples were prepared as listed in section 3.5.2.

3.7. Physicochemical Analysis of Zeolite

There are several widely accepted methods for the identification of crystalline compounds including differential thermal analysis, x-ray diffraction analysis, and infrared spectroscopy. The primary zeolite used in this study, mordenite, was tested by x-ray diffraction and infrared spectroscopy for purity of composition.

3.7.1. X-ray Diffraction Analysis

Zeolite samples were prepared for x-ray diffraction analysis by the use of a mortar and pestle to finely grind the zeolite into a smooth powder with a mesh size of 120+. Approximately 0.500 g of zeolite was analyzed in the Phillips' X'Pert X-ray Diffractometer using a $\text{CuK}_{\alpha 1}$ radiation (See Appendix A, page 57 for instrument parameters).

3.7.2. Infrared Spectroscopy

The samples of zeolite were prepared for infrared spectroscopy with potassium bromide zeolite was present in 1% by weight. The sample was finely ground in a mortar and pestle and pressed into a pellet disc under 2000 psi for 15 seconds. The zeolite sample was analyzed by Fourier-Transform on Nicolet Impact 400D FT-IR Spectrometer (See Appendix A, page 57 for a list of instrument parameters).

3.7.3 Chemical Analysis of Mordenite

A 0.1000 g sample of mordenite was treated with 10.0 ml solution of 1% HF (hydrofluoric acid) to digest the zeolite. The digested sample was analyzed for uranium and calcium concentrations using ICP/MS.

3.8 Chemical Stability of Mordenite

The purpose of this study is to determine the stability of the mordenite at the different pH conditions and to ascertain the effects of the pH on the alumino-silicate framework of the zeolite. A 1.000 g sample of mordenite was mixed with 200.0 ml of each of the buffered and unbuffered solutions at the three pH conditions, namely 3.00, 4.00, and 5.50. The mordenite samples were analyzed for stability by measuring the leachability of aluminum from the framework of the zeolite. The mordenite stability tests were conducted in 250 ml polyethylene vials and placed on a reciprocating shaker for 24 and 72 hours, respective to the adsorption study. The samples were removed from the shaker and filtered by gravity filtration using Whatman 2 filter paper (Whatman No. 6) overnight. The eluent was then transferred to a clean 250 ml polyethylene vial. For ICP-MS analysis, the filtrate of the samples was diluted to the ppb range in 10.0 ml volumetric flasks using a 1% HNO_3 solution. The residue was allowed to dry overnight and then stored in a 20.0 ml polyethylene vial for x-ray diffraction analysis.

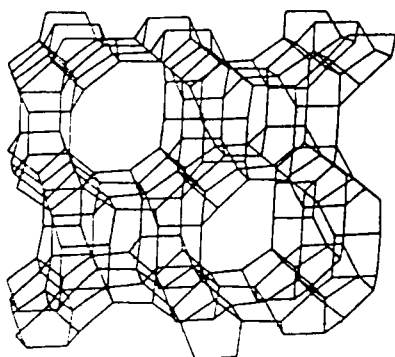
CHAPTER 4

RESULTS AND DISCUSSION

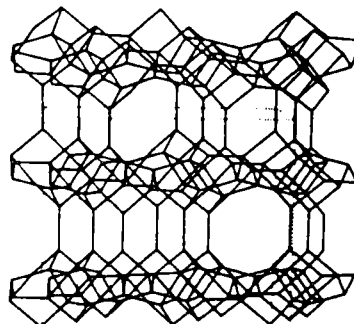
4.1 Zeolite Selection

The axial diameter of the UO_2^{2+} cation is 0.6 nm,⁹ therefore zeolites with pore sizes of 0.6 nm and greater were selected. Several large pore zeolites were selected for both the batch and column percolation trials. The natural zeolite, clinoptilolite (0.76 x 0.30 nm) and synthetic zeolites X and Y (0.74 nm each), L (0.71 nm), and mordenite (0.70 x 0.65 nm) were evaluated for the uptake of UO_2^{2+} .¹⁹ Figure 1 and Figure 2 shows the frameworks and the pore openings of these zeolites, respectively.

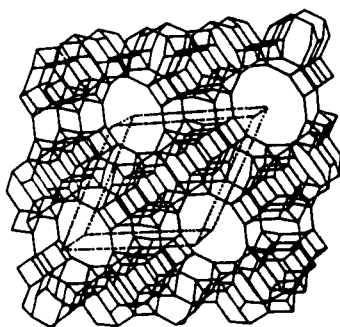
Figure 1. Framework of zeolites used in sorption studies.²⁴



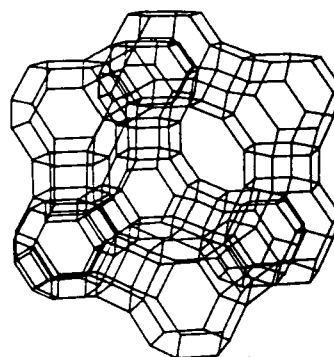
A. Mordenite framework viewed along [001]



B. Clinoptilolite framework viewed along [001]

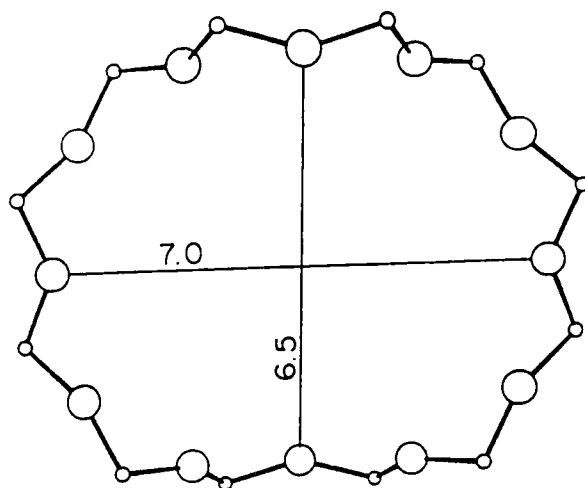


C. Zeolite L framework viewed along [001]

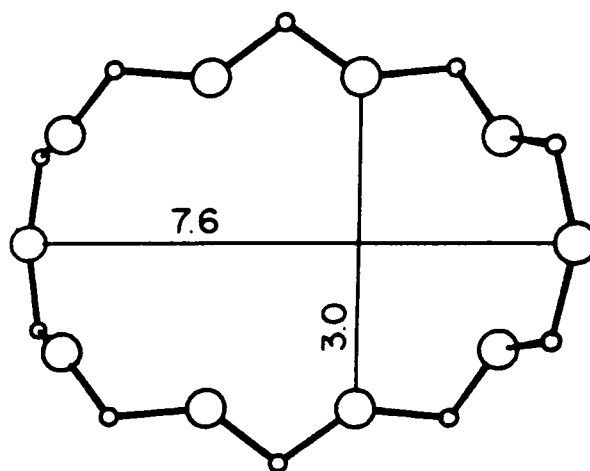


D. Zeolites X and Y framework viewed [111]

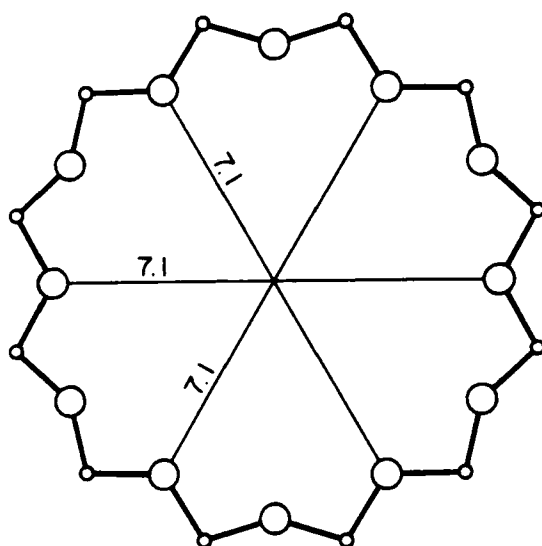
Figure 2. Pore openings of zeolites used in sorption studies.²⁴



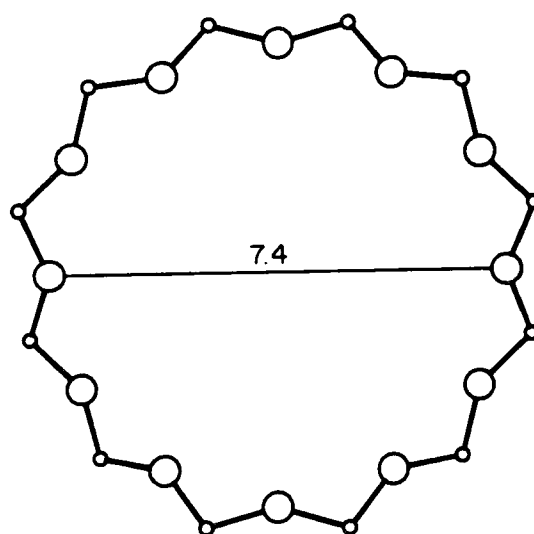
A. Mordenite pore opening
12-member ring viewed along [001]



B. Clinoptilolite pore opening
10-member ring viewed along [001]



C. Zeolite L pore opening
12-member ring viewed along [001]



D. Zeolites X and Y pore opening
12-member ring viewed along [111]

4.2 Soil Analysis

Table 3 shows that soil pH was determined to be in the range between 7.69 to 8.00 pH units. The variation of these values are attributed to the variation in the soil samples as well as equilibration time. Most standard methods of soil pH measurements only require 30 to 60 minutes of equilibration time.^{20,21} The soil was analyzed for both exchangeable cations and cation exchange capacity.

Table 3. Soil pH Measurements

Equilibration Time	Trial 1 pH	Trial 2 pH	Trial 3 pH	Average pH
1 hr	7.59	7.95	7.53	7.69
8hr	7.91	7.76	8.01	7.89
24 hr	7.96	7.99	8.07	8.00

4.2.1 Soil Cation Analysis

The 0.1000 g soil samples treated with the pH buffered and unbuffered solutions were analyzed via ICP/MS for all elements (metals) present in solution after three days. The sensitivity of the ICP/MS for this study provided a quantitative analysis. Most of the samples contained calcium at a concentration between 150 to 400 ppm and magnesium between 5 to 25 ppm. These results correlate with the findings of Cunnane et. al. for the most abundant cations present in the Fernald soil.¹ The internal composition of the ICP/MS will not allow for accurate analysis of sodium, potassium, and silicon. The analysis of these elements could only be done with background subtraction on ICP/MS and were present in less than 100 ppb concentration as soluble cationic species.

4.2.2 Soil Exchangeable Cations

The standard ammonium saturation method (Appendix B, page 59) was utilized to determine the amount of exchangeable cations present in the soil. This method is widely used because it is highly buffered and the ammonium is easily determined.²⁰ The cation exchange capacity (CEC) for this particular soil was found to be 30 milliequivalents per 100 g soil; where CEC is defined as:

$$\text{CEC} = \sum \text{mEq exchangeable cations per 100 g soil.}^{20}$$

The CEC was measured by the titration of ammonium present in solution after saturation of the soil sample with a 10% NaCl solution (acidified with HCl to 0.005N).

4.3 Adsorption Studies

The adsorption studies provided information on the kinetics of the uptake of uranium on the zeolites and soil. The results were primarily dependent on the ratio of sorbent to cation concentration in solution. The pH and time were also important factors.

4.3.1 Column Studies with Uranium in Solution

Using a matrix of 5% zeolite + 95% soil (in a 1:1 soil/sand mixture), with 23.8 and 119 ppm U solutions as influent, mordenite and LZY showed no breakthrough at >1 ppm U up to 600 bed volumes, whereas both clinoptilolite and 13X showed breakthroughs at > 1 ppm U as early as the first 10 bed volumes of the effluent (Figure 3). For 119 ppm U solution, clinoptilolite showed full breakthrough after 50 bed volumes. At 24 ppm U the breakthrough was slower, occurring after 300 bed volumes for both clinoptilolite and 13X demonstrating that both are less effective than the other zeolites tested for the uptake of uranium.

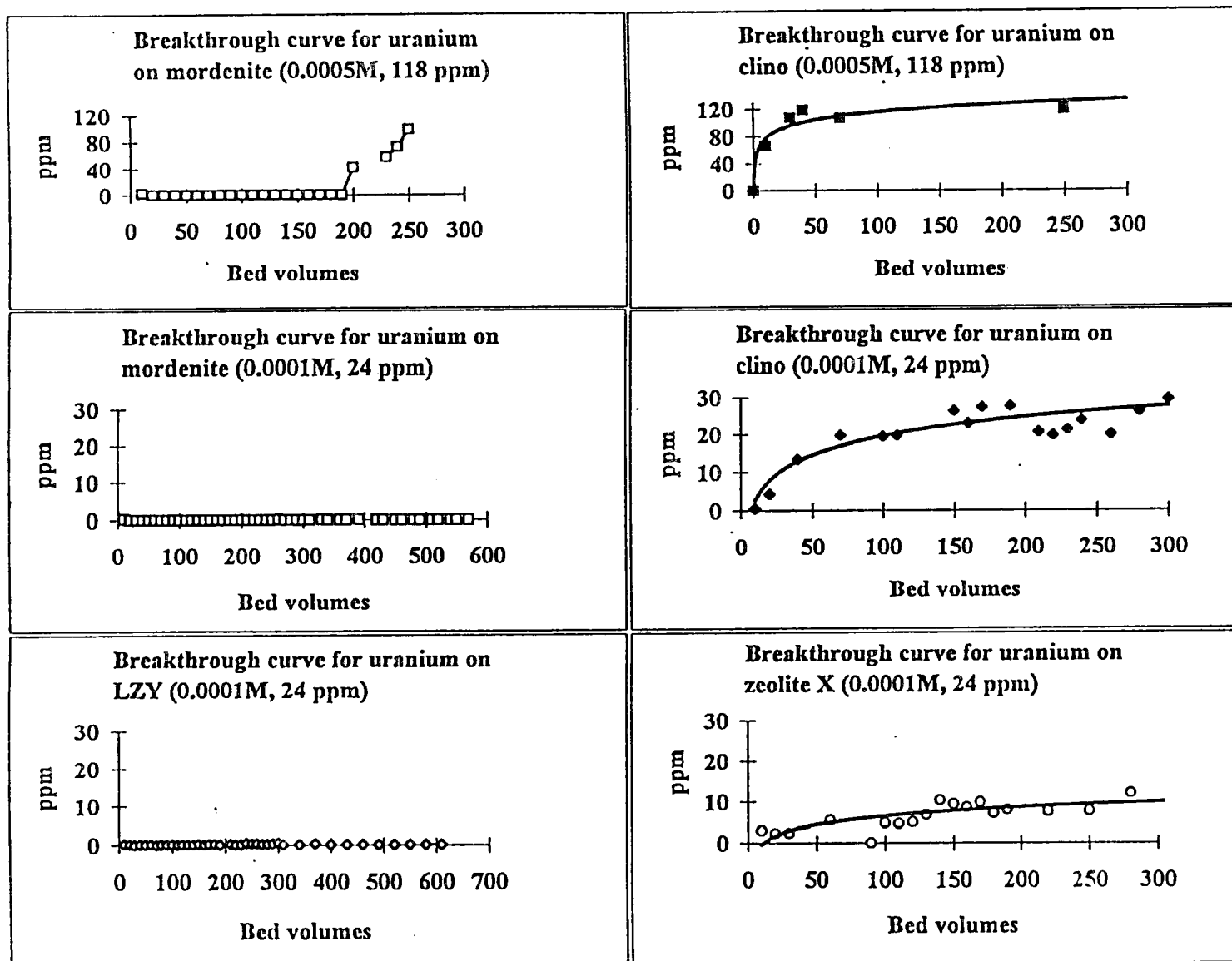


Figure 3. Breakthrough curves of preliminary column studies

4.3.2 Column Studies with Uranium in Soil

Double deionized water was used to leach uranium from the uranium loaded soils in the column study with the matrix of 5% zeolite + 95% soil (in a 1:1 soil/sand mixture). Figure 4A shows the 50 ppm uranium loaded soil system column study results. The rate of leaching of uranium from the soil was much less than the maximum concentration of uranium (9.5 ppm) that could be expected in the first 10 bed volumes (20 ml). This was probably due to water not being a very good leachate for uranium from these soils and the inconsistent flow rates of solution through the column.

Figure 4A. Uranium concentration in effluent from column studies on 50 ppm uranium loaded soil.

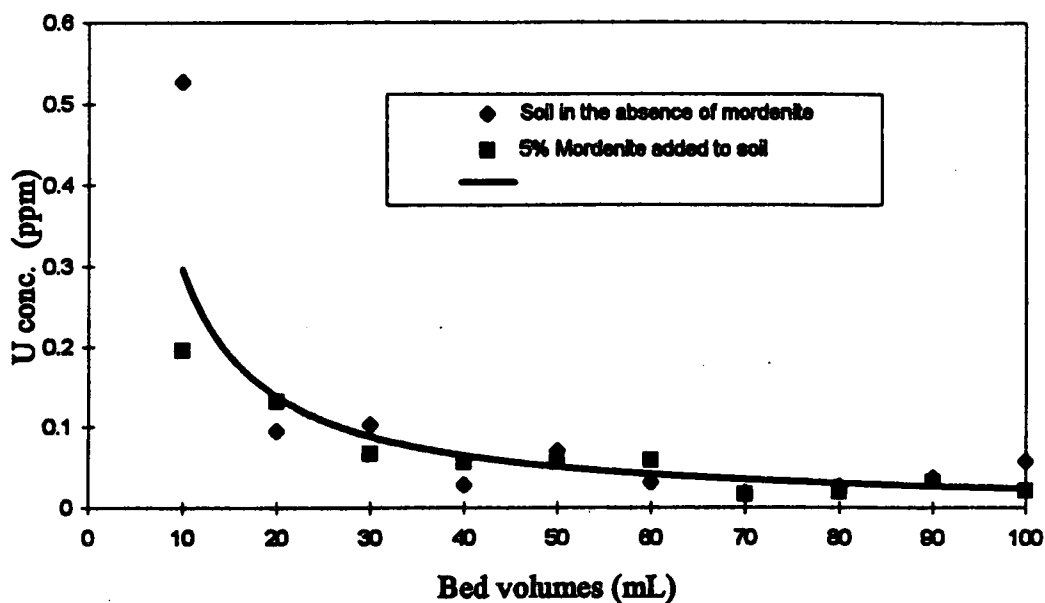
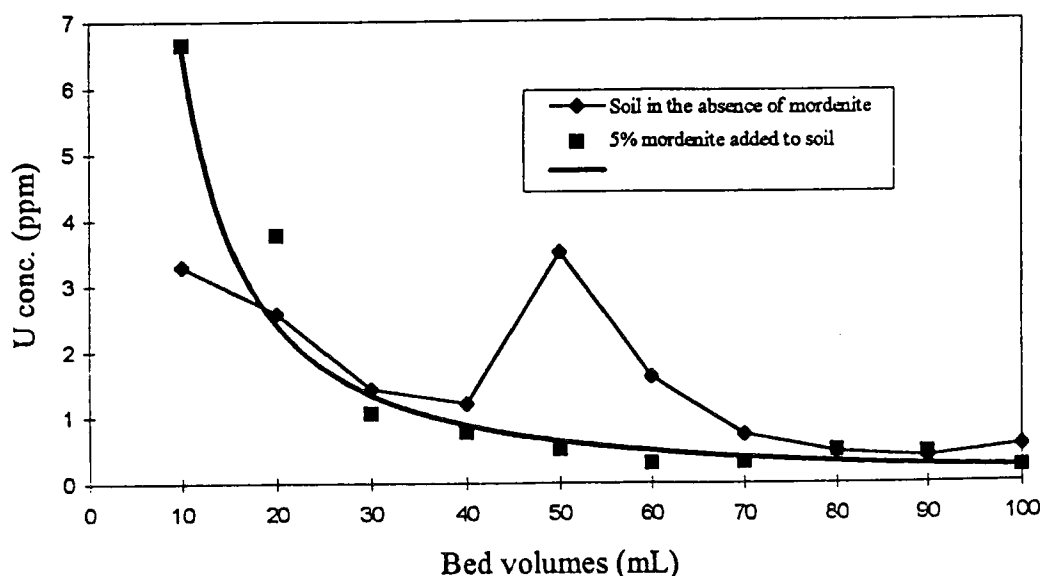


Figure 4B shows the 500 ppm uranium loaded soil system. Once again the column system demonstrated inconsistent flow rates which caused poor rates of uranium leaching from the column and periodic jumps in the data due to extended amounts of time for the 10 bed volumes (20 ml) to flow through the column.

Due to the flocculation of the FEMP-like soil and the resulting poor hydraulic conductivity, further column studies were suspended in favor of batch studies.

Figure 4B. Uranium concentration in effluent solution from column studies on 500 ppm uranium loaded soil.



4.3.3 Batch Studies

Table 4 shows results of preliminary batch studies with uranium in solutions of varying uranyl acetate concentration, mordenite was shown to reduce 238 ppm U to 40 ppm U in 48hrs, while reducing a 119 ppm U solution to ~ 5 ppm U in 24hrs. Zeolite K-L

Table 4. Performance of various zeolites in uranium uptake in batch studies.

Zeolite	Initial Uranium conc. (ppm)	Final Uranium conc. (ppm)	Percentage Uptake (%)
Mordenite	238	40	84
Mordenite	119	2	98
K-L	119	3	96
LZY	24	1	96
Clinoptilolite	24	15	38

gave similar results for the 119 ppm U trial and reduced the 24 ppm U solution to ~ 4 ppm U in 24hrs. On LZY, a 24 ppm U solution was reduced to ~ 1 ppm U in < 8hrs. With clinoptilolite however, a 24 ppm U solution was reduced only to ~ 15 ppm U even after five days. These results demonstrate that mordenite, LZY, and K-L are promising materials for the uptake of uranium. Mordenite was selected for further study because of performance in the uptake of uranium from solution and that it can be obtained as a naturally occurring as well as inexpensive mineral for potential scale-up applications.

Uranium uptake was found to be dependent on solution pH, amount of sorbent, and cation concentration. The pH was determined to be a major contributing factor in uranium uptake based upon its affect on both the soluble UO_2^{2+} and the zeolite. With any changes in the pH of the system, uranium can exists in solution as other soluble hydrolyzed species as well as UO_2^{2+} . Thus, further study was directed to be pH based with the use of buffer solutions and solutions with the pH adjusted by HNO_3 to a desired range.

4.3.4 pH Controlled Batch Studies

The influence of pH on uranium ion speciation was suspected to be responsible for the variation of uranium binding with the zeolite. In solution, uranium can be present as ions corresponding to four states of oxidation: 3+, 4+, 5+, and 6+.¹² At higher pH more sites may be available for UO_2^{2+} uptake but above pH 5.9 uranium may exist as insoluble U_3O_8 which would precipitate out of solution and not be adsorbed.¹²

4.3.4.1 Citric Acid Buffer System

Francis et. al. found citric acid to be very useful in leaching uranium out of soils.²² Also, citric acid buffer solutions can exist in pH range of $\sim 2.13 - 7.40$ thus making it an excellent choice for the pH study. Uranium uptake was studied in a three day batch study for 0.001M UA (238 ppm U) at pH 3.00, 4.00 and 5.00 using 0.1000 g mordenite per 20 ml solution. The buffer solution maintained the pH to within ± 0.05 points for the samples containing mordenite only. The samples containing the soil exhibited jumps in the pH of 0.30 - 0.75 pH units. Mordenite was found to be non-effective in the uptake of uranium in these buffer systems. The uptake was generally less than 30 ppm U and as little as 5 ppm U in solutions containing both the soil and mordenite (Figure 5). The complex nature of the soil as well as its ion exchange capabilities are to be studied further to fully understand the soil's contribution to the reduced effectiveness of the mordenite. It is also suspected that the formation of uranyl citrate complexes inhibited the adsorption of uranium into the channels of the zeolite. Therefore, a new buffer solution system was recommended, one that would not form large complexes with the UO_2^{2+} such that adsorption of uranium via the zeolite would be permitted.

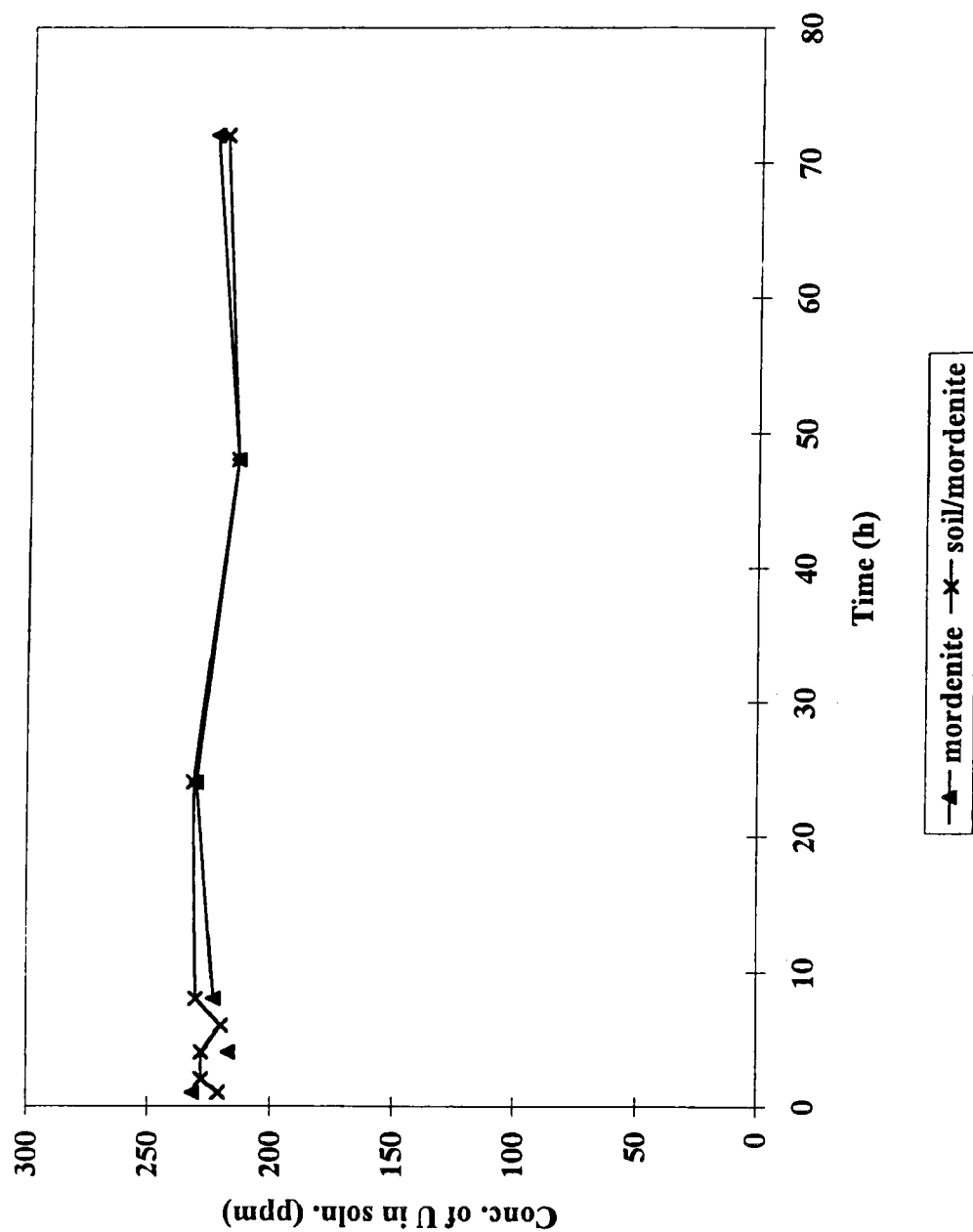


Figure 5. Uptake of uranium by mordenite vs. soil/mordenite from a citric acid buffered solution at pH 5.00.

4.3.4.2 Acetic Acid Buffer System

Studies were subsequently conducted using a sodium acetate/acetic acid buffer system and uranium concentrations of 23.8 and 238 ppm. To determine the effects of the soil on uranium uptake as well as pH, in this batch study the soil and mordenite were not placed together in the sample vials. All further studies used this buffer system.

4.3.4.2.1 pH 5.50 Batch Study

As with the first buffered pH study, the soil caused major jumps in the pH in the range of 2.00 - 3.00 pH units, whereas the samples containing mordenite showed a reduced pH of ~ 0.20 - 0.30 points for both the buffered and unbuffered samples in the pH 5.5 study for 23.8 and 238 ppm U concentrations (Figure 6). Mordenite demonstrated a 93 percent uptake for the 23.8 ppm U buffered system (Figure 7) and exhibited a 50 percent uptake of uranium in the 238 ppm U (Figure 8). The soil had a markedly lower adsorption for these buffered systems with only a 35 to 40 percent uptake for both the 23.8 and 238 ppm U solutions, respectively.

Figure 7 also shows the uranium uptake by mordenite in the 23.8 ppm U unbuffered system. Mordenite demonstrated a 78 percent uptake versus a 40 percent uptake by the soil. For the 238 ppm U concentration in this buffer system (Figure 8), the soil and mordenite performed similarly with a 60 percent uptake for the soil and a 68 percent uptake for the zeolite. These results indicate that for a low concentration of uranium in solution (10^{-4} M) with the pH remaining fairly constant at a pH of 5.5, mordenite will effectively reduce the U concentration by greater than 85 percent. These two specific conditions have been shown to be the most effective in the adsorption of U from solution by mordenite and may be the optimal conditions for uranium adsorption via ion exchange for mordenite.

Figure 6. Comparison of variation of solution final pH with time for uranium uptake on mordenite vs. soil from 23.8 and 238 ppm U solutions of initial pH 5.5.

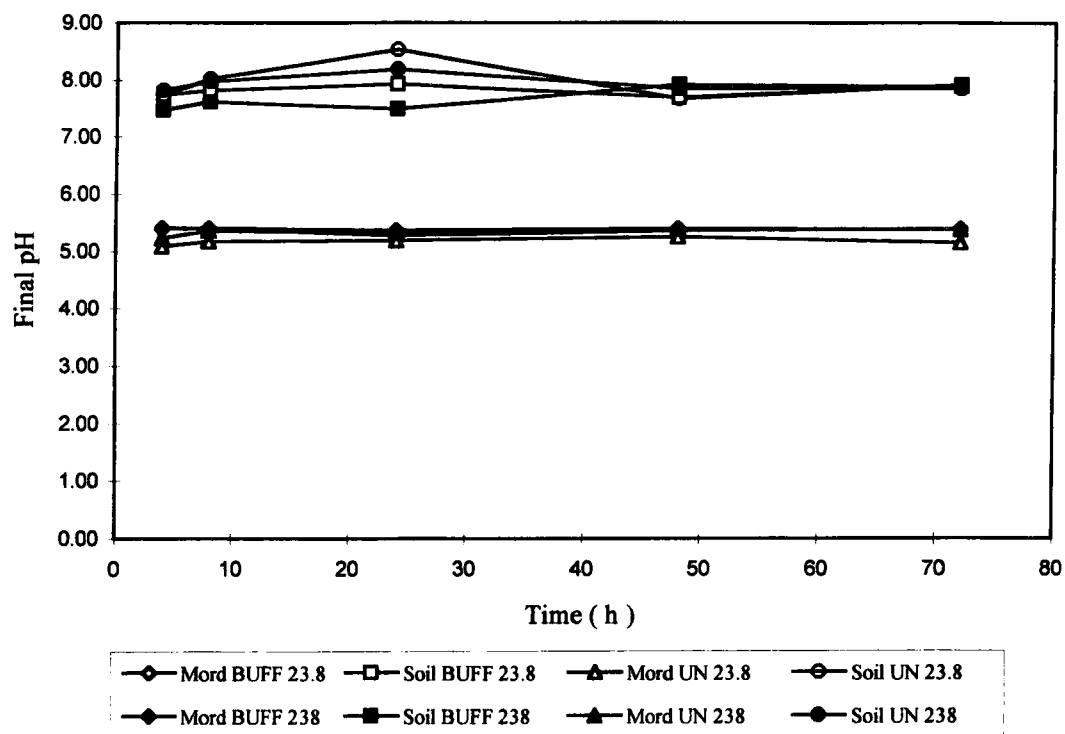


Figure 7. Comparison of uranium uptake on mordenite vs. soil from 23.8 and 238 ppm U buffered and unbuffered solutions of initial pH 5.5.

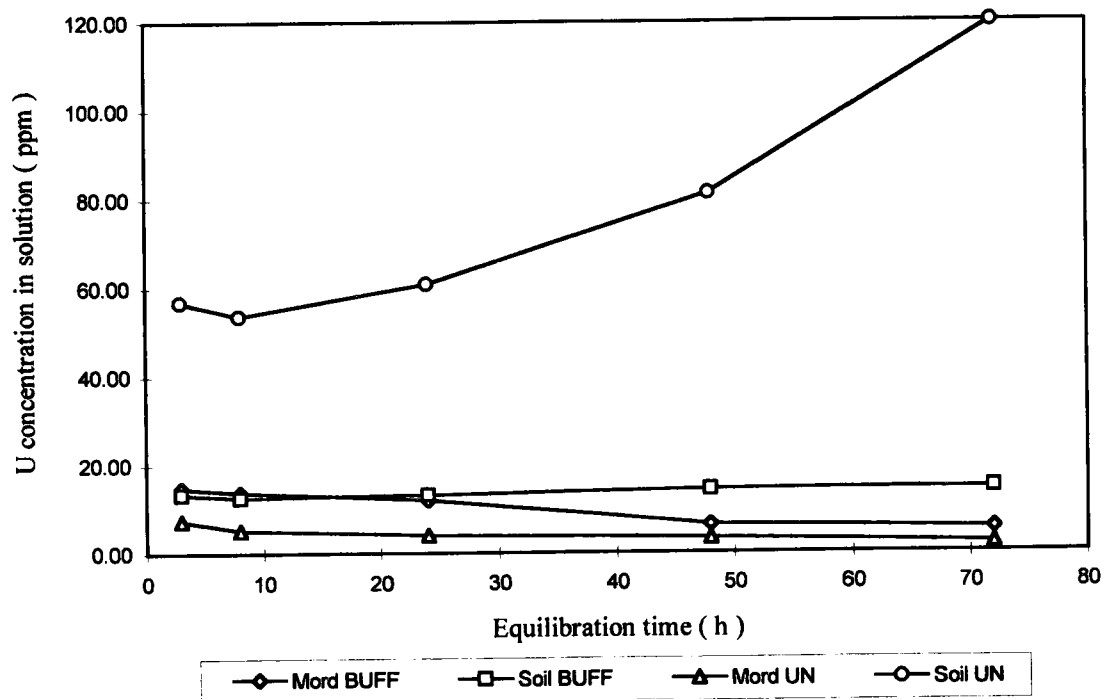
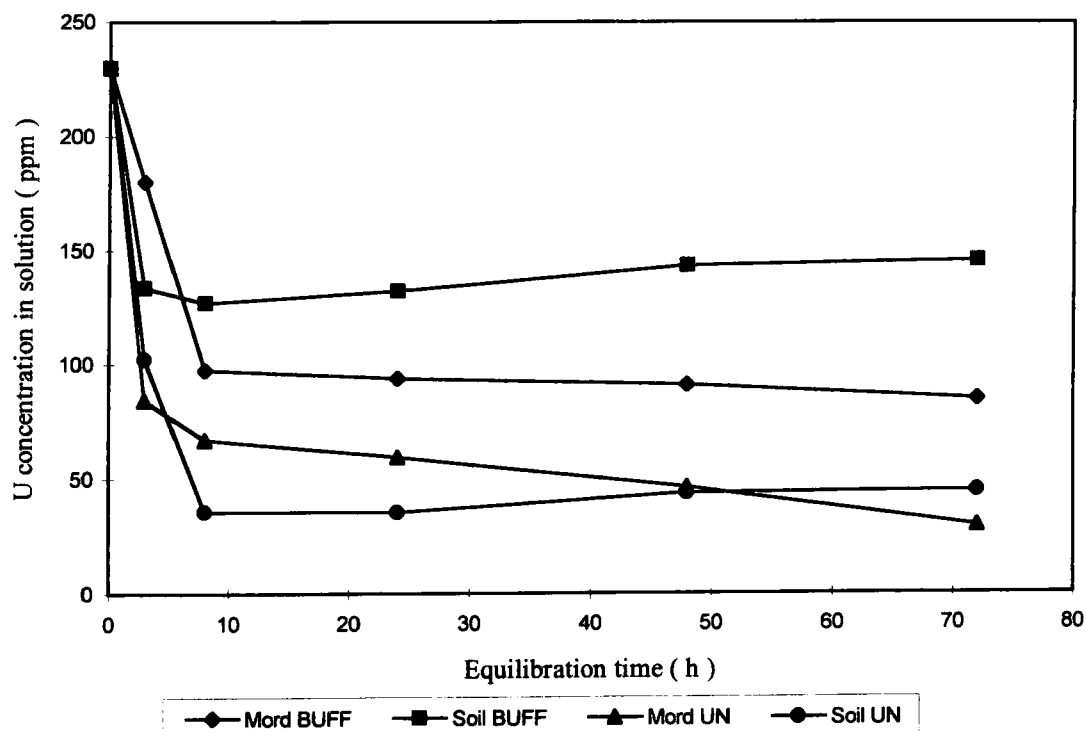


Figure 8. Comparison of uranium uptake on mordenite vs. soil from 238 ppm U buffered and unbuffered solutions of initial pH 5.5.



4.3.4.2.2 pH 4.00 Batch Study

For the buffered system, mordenite showed only a 39 percent uptake of U from the 23.8 ppm U solution compared to a 37 percent uptake by the soil (Figure 9). In Figure 10 the uranium uptake was much less in the 238 ppm U concentration system, with less than 20 percent uptake for mordenite and 5 percent for the soil. These results imply that a sodium acetate/acetic acid buffer system at pH 4.0 does not facilitate uranium adsorption from solution indicating that there may be less uranyl ions present in solution under these conditions.

Figure 9. Comparison of uranium uptake on mordenite vs. soil from 23.8 ppm U buffered and unbuffered solutions at initial pH 4.00.

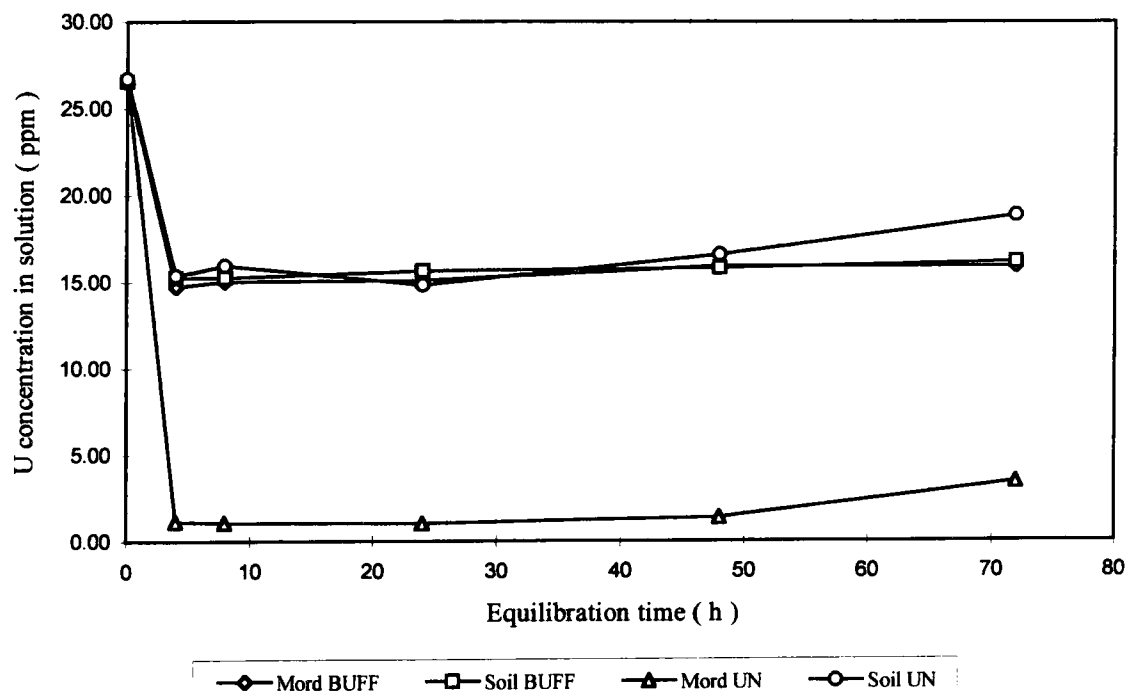
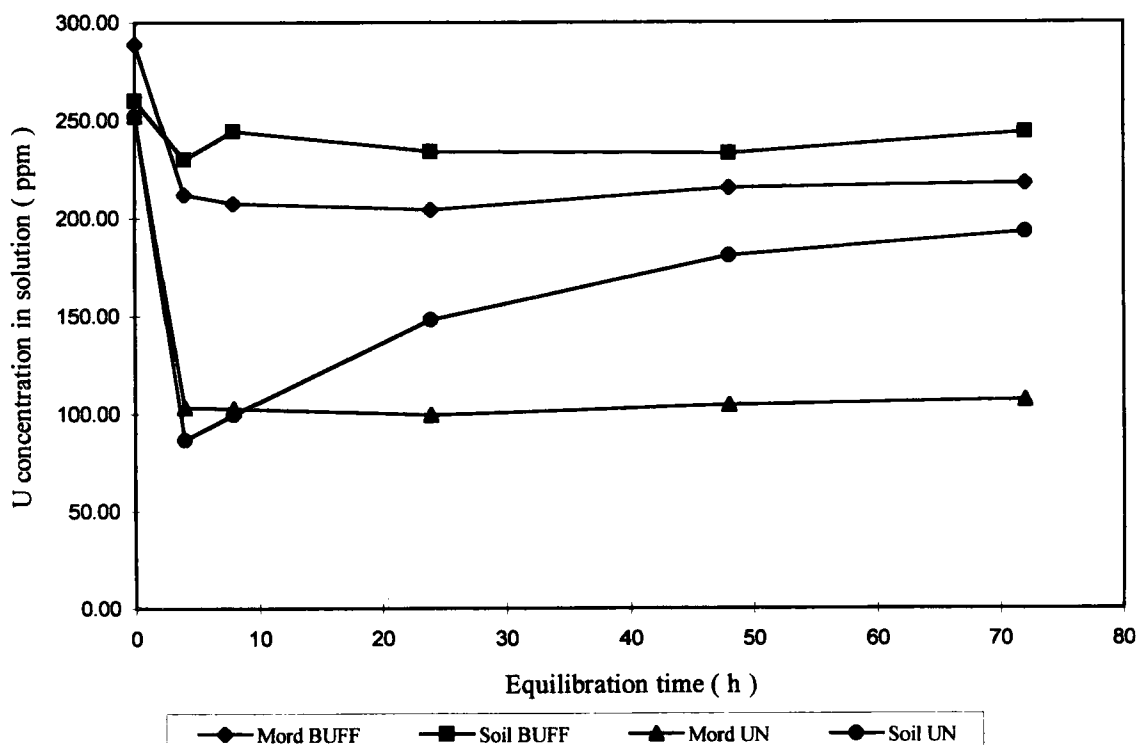


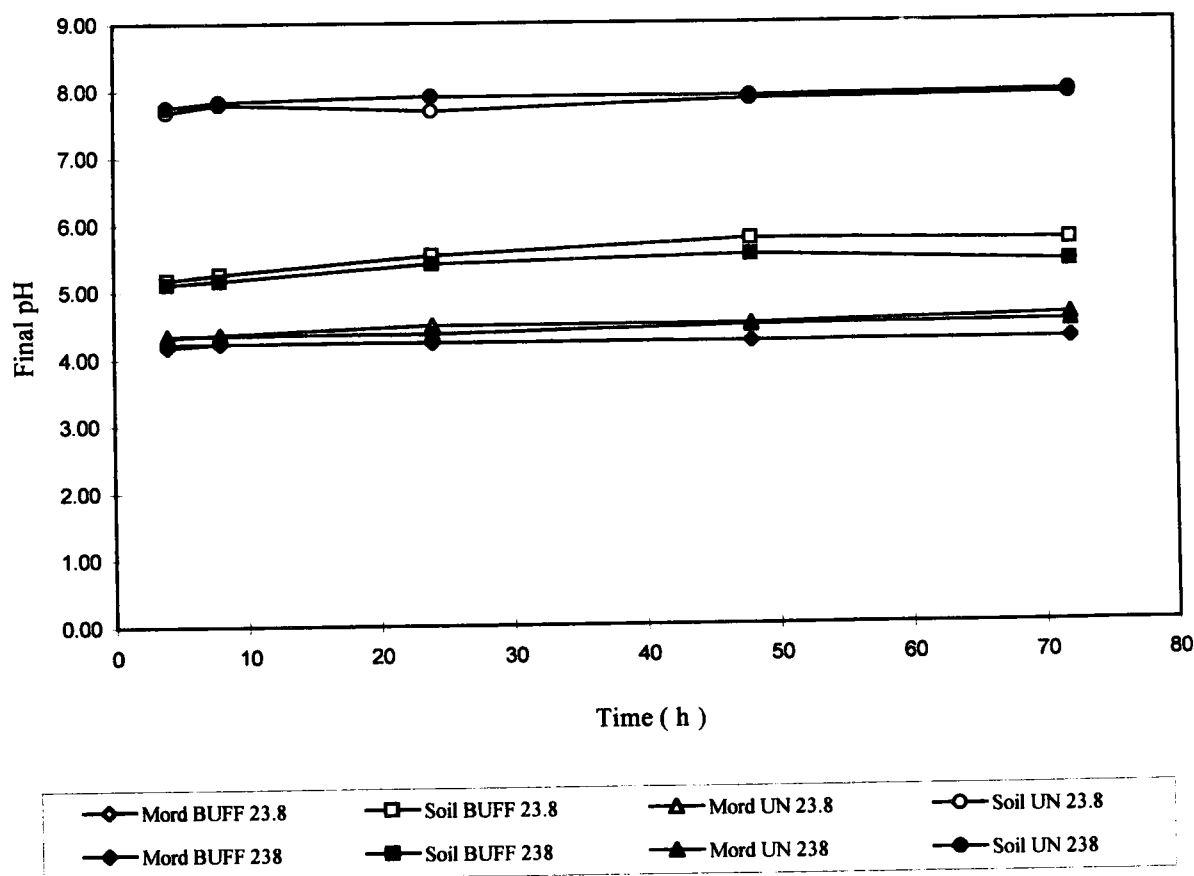
Figure 10. Comparison of uranium uptake on mordenite vs. soil from 238 ppm U buffered and unbuffered solutions of initial pH 4.00.



In contrast to the buffered system, Figure 9 also shows much higher U uptake in the unbuffered conditions. Mordenite had a 87 percent and a 62 percent uptake for the 23.8 and 238 ppm U (Figure 10) concentrations respectively whereas the soil had 25 and 20 percent uptake for the same solutions.

The increase in pH was small (0.10 - 0.30) for the samples containing mordenite for both the buffered and unbuffered solutions at 23.8 ppm U concentration (Figure 11). For samples containing the soil, the buffered solution exhibited a 1.0 - 1.3 pH unit increase and the unbuffered solution had an increase in pH of 3.5 - 4.0 pH units (Figure 11).

Figure 11. Comparison of variation of solution final pH with time for uranium uptake on mordenite vs. soil from 23.8 and 238 ppm U buffered and unbuffered solutions of initial pH 4.00.



4.3.4.2.3 pH 3.00 Batch Study

Figure 12 and Figure 13 show the percentage of uranium uptake at pH 3.00 for mordenite and the soil in the buffered system. This uptake was considerably lower than any of the other sodium acetate/acetic acid buffer systems with an uptake of 20% or less for both the mordenite and the soil. In the unbuffered 23.8 ppm U concentration, mordenite had a 78 percent uptake (Figure 12) and the soil demonstrated a maximum uptake of 39 percent in the 238 ppm unbuffered system (Figure 13). The changes in pH

Figure 12. Comparison of uranium uptake on mordenite vs. soil from 23.8 ppm U buffered and unbuffered solutions of initial pH 3.00

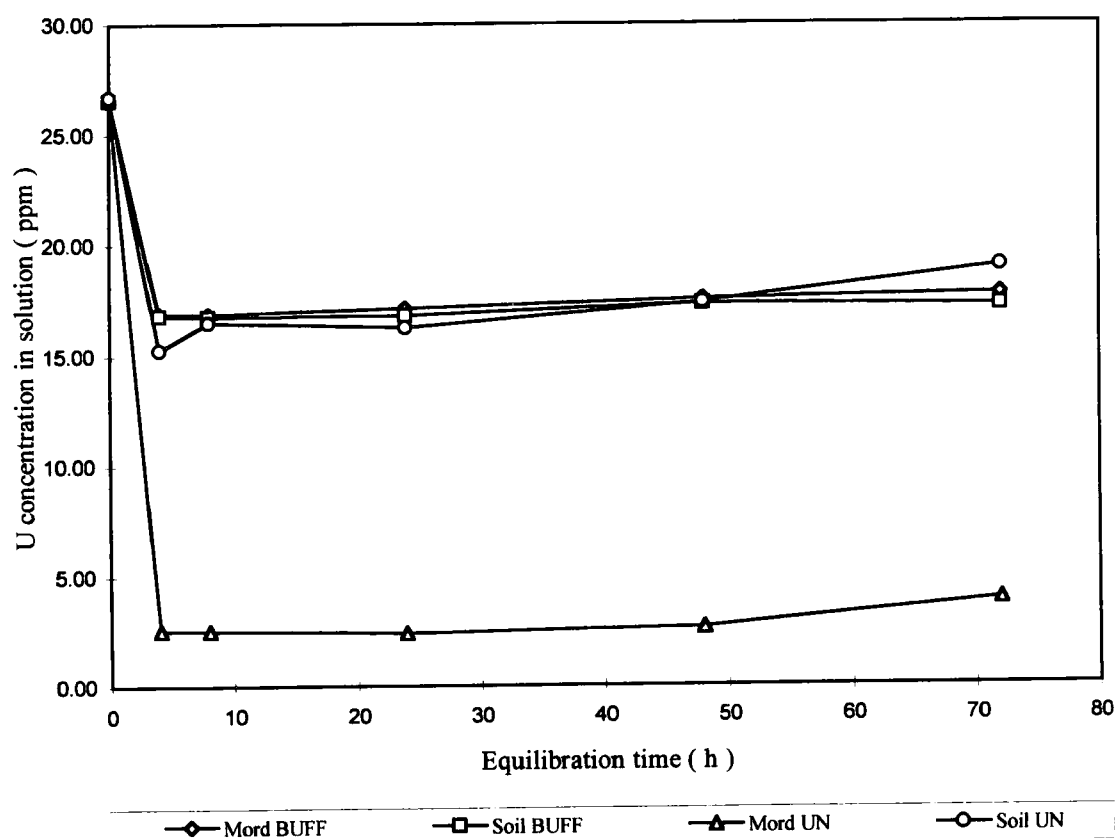
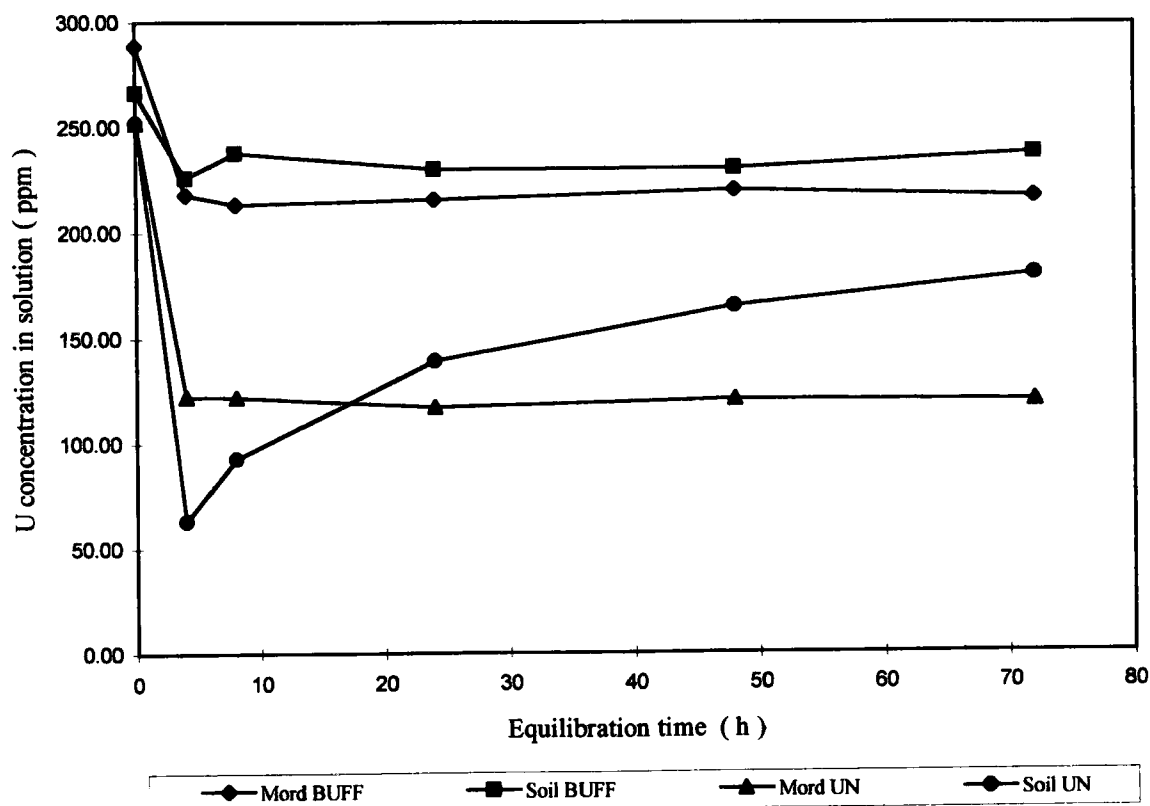


Figure 13. Comparison of uranium uptake on mordenite vs. soil from 238 ppm U buffered and unbuffered solutions of initial pH 3.00



were consistent with the findings in the other pH batch studies (Figure 14). The poor uranium uptake can be attributed to the low pH of the solutions and the adverse affects of the lower pH on the soil. The excess of acetic acid in the buffered solutions, which provided an increase in the hydrogen ion concentration, decreased the mordenite percentage uptake of uranium by the H^+ ions competing for the mordenite active sites. At pH 3.00, the buffer has a reduced effectiveness by being more than one pH unit out of the range of the pK_a of the buffer system.

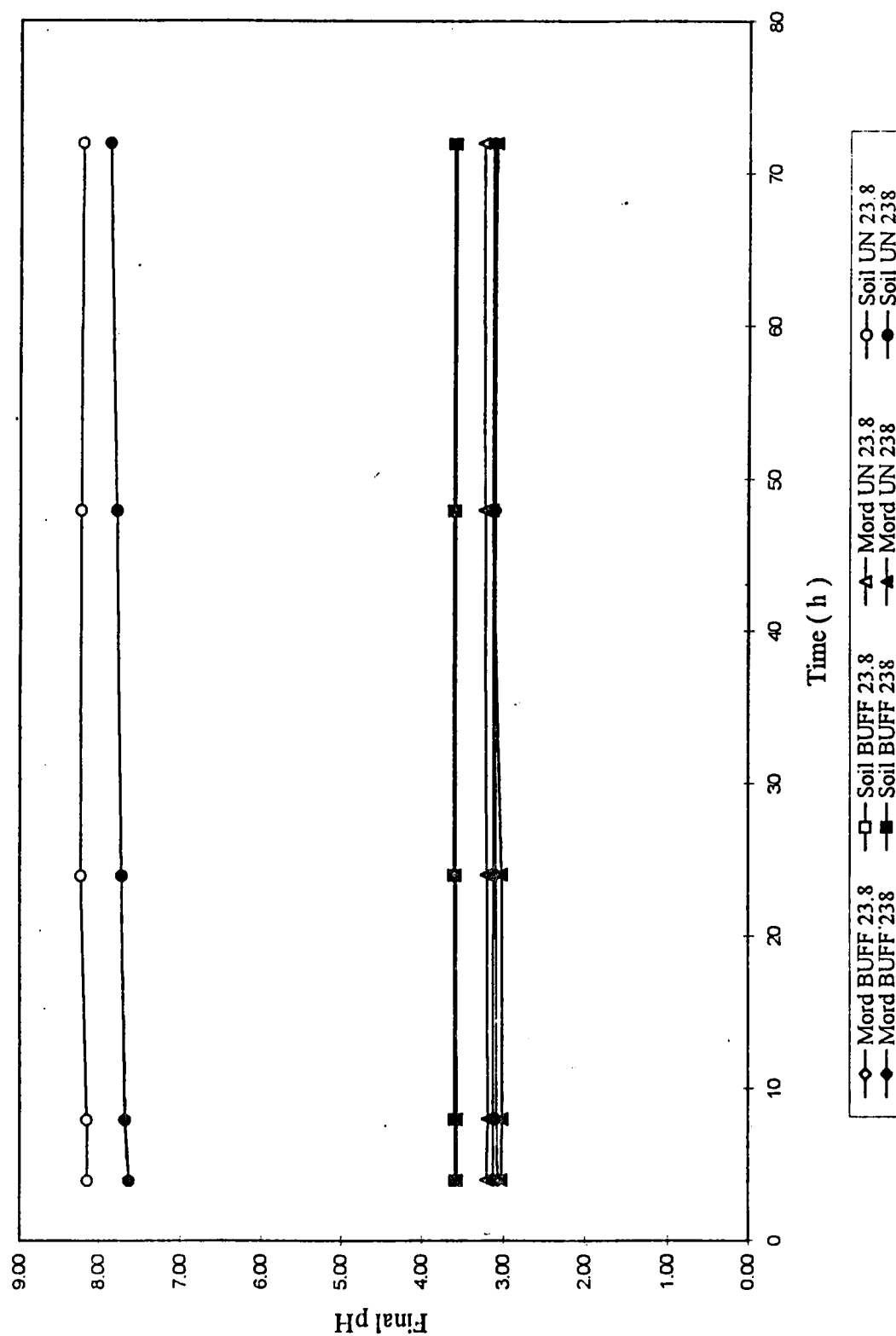
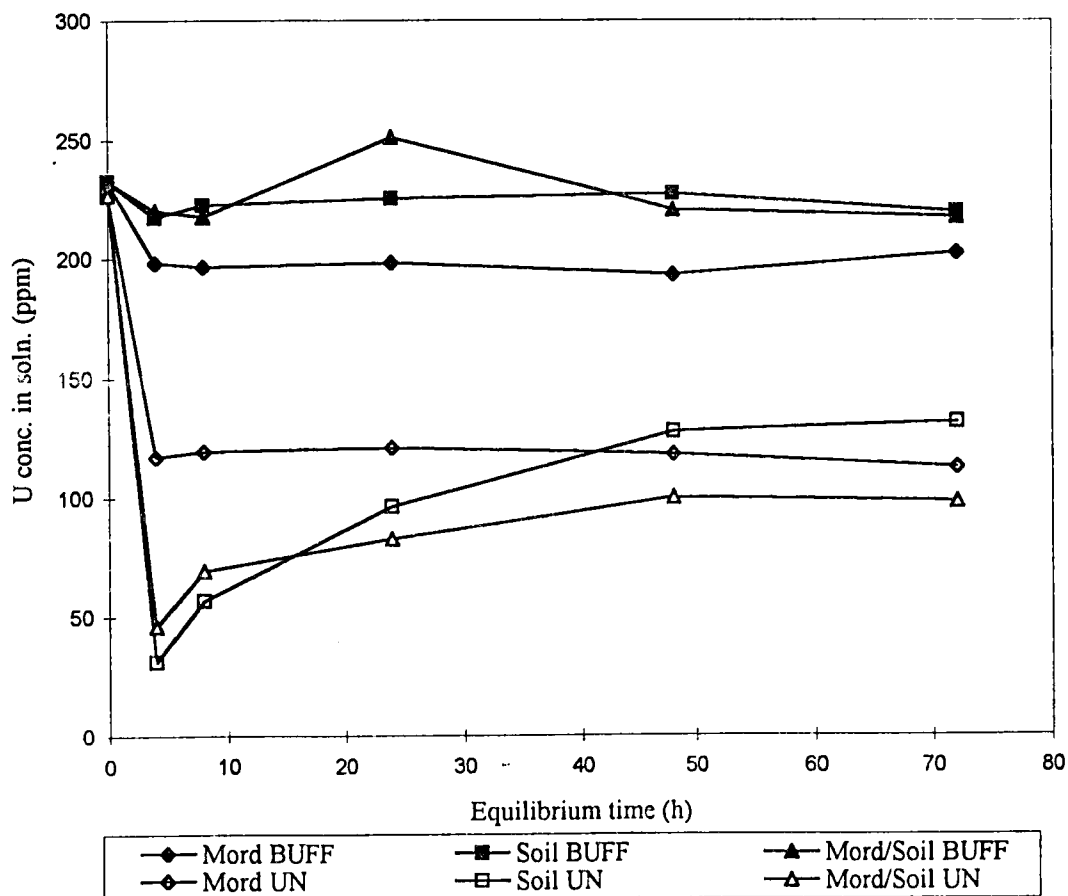


Figure 14. Comparison of variation of solution final pH with time for uranium uptake on mordenite vs. soil from 23.8 and 238 ppm U buffered and unbuffered solutions of initial pH 3.00.

4.3.5 Mordenite vs. Soil Competitive Adsorption Batch Study

In this batch study, the mordenite and soil were placed in direct competition for uranium adsorption. Figure 15 show the performance of mordenite at pH 3.00 with the best cases of uranium uptake was mordenite/soil unbuffered and mordenite unbuffered. In the absence of buffer, the increase of uranium uptake can be rationalized by a lesser concentration of sodium or hydrogen ions present in the buffer competing for the mordenite active sites. The uranium uptake is an increase of twenty to thirty percent over the uptake in the buffered solutions.

Figure 15. Comparison of uranium uptake from 238 ppm U buffered and unbuffered solutions.



For pH 4.00 (Figure 16), similar results were obtained. The mordenite and mordenite/soil unbuffered demonstrated the best uranium uptake removing 160 and 120 ppm U from solution, respectively. The unbuffered system has the drawback of not being able to maintain pH, which is critical as the pH of the solution determines which uranium species are present in solution.

Figure 16. Comparison of uranium uptake from 238 ppm U buffered and unbuffered solutions with initial pH 4.00.

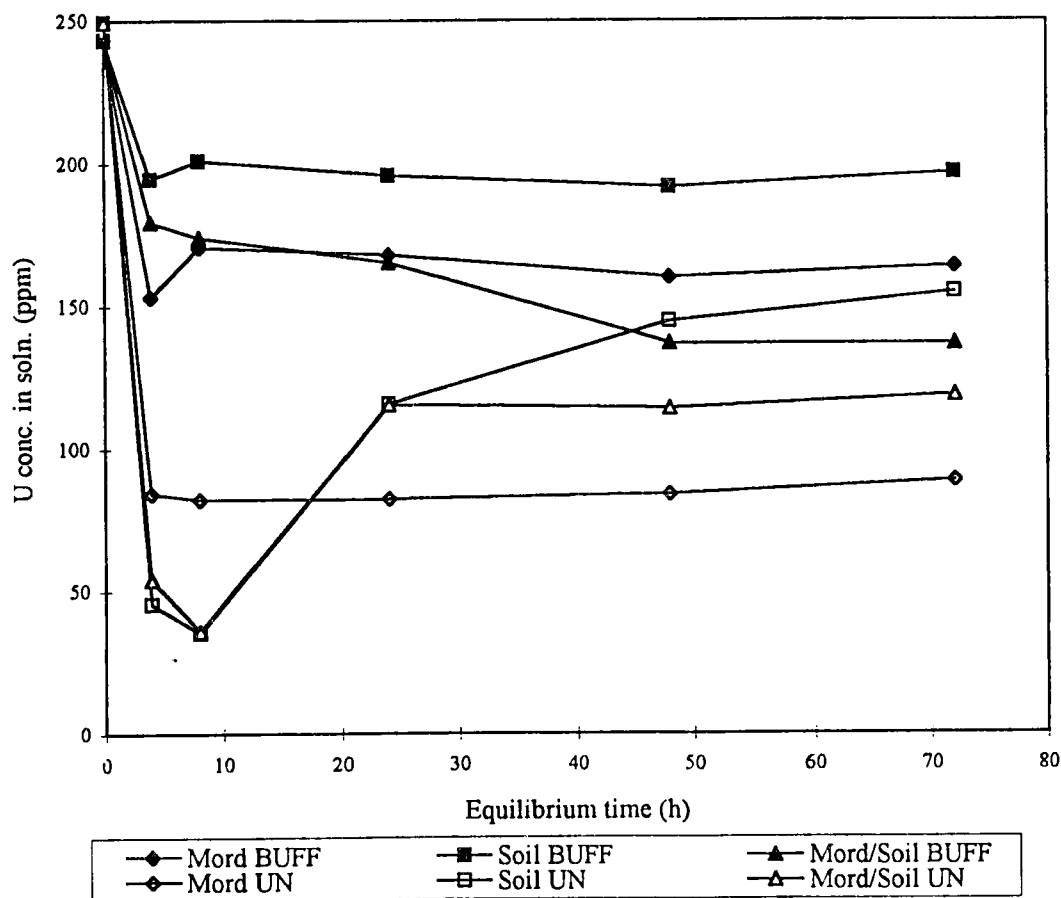
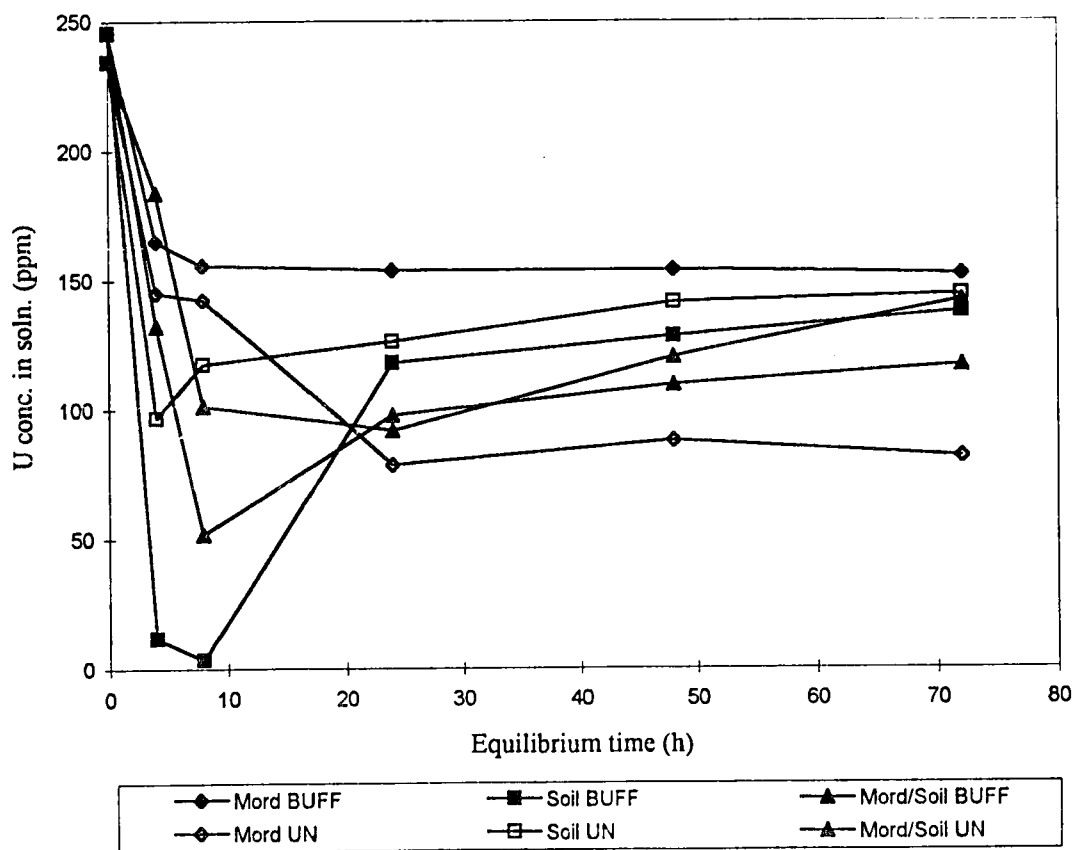


Figure 17 shows the uranium uptake at pH 5.50 where once again the mordenite unbuffered demonstrated the most uptake of 165 ppm. The pH jumps observed in previous experiments were consistent here as well. The buffered system maintains the pH in the presence of the soil whereas the unbuffered does not. In either case, the uranium adsorbed by the soil is seen to redissolve over time while mordenite retains the uranium.

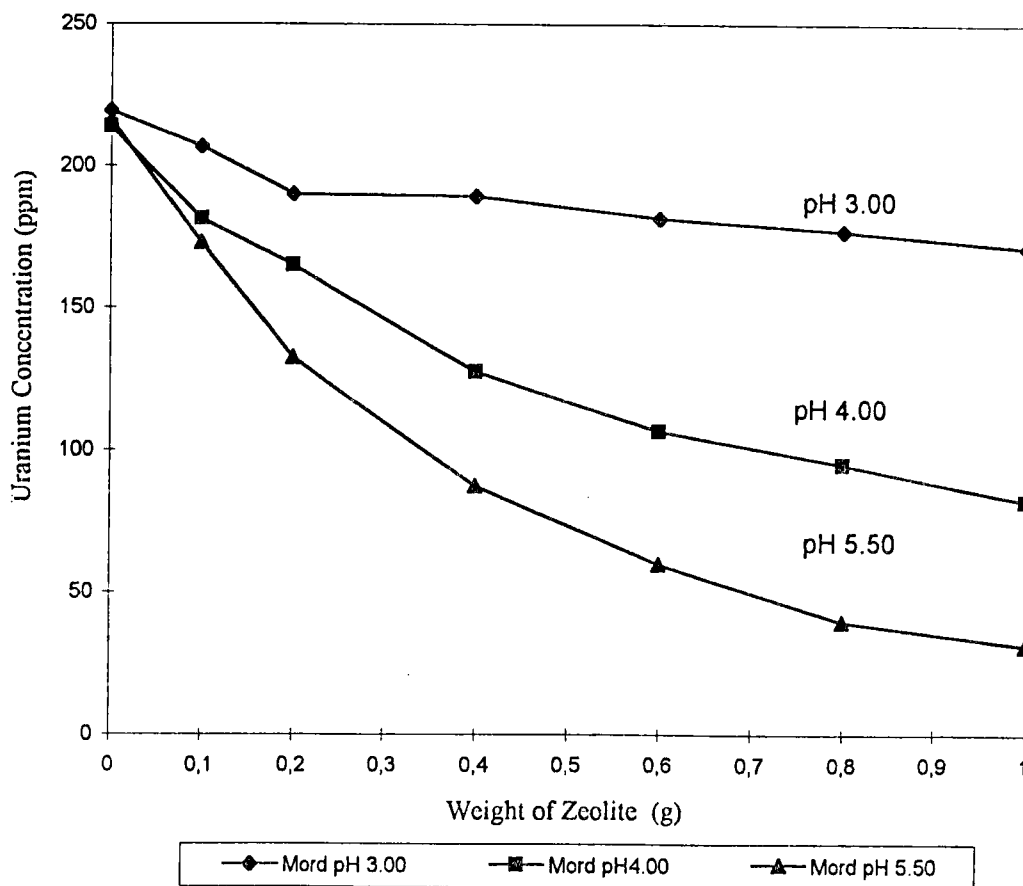
Figure 17. Comparison of uranium uptake from 238 ppm U buffered and unbuffered solutions with initial pH 5.50.



4.3.6 Optimum Uranium Uptake on Mordenite

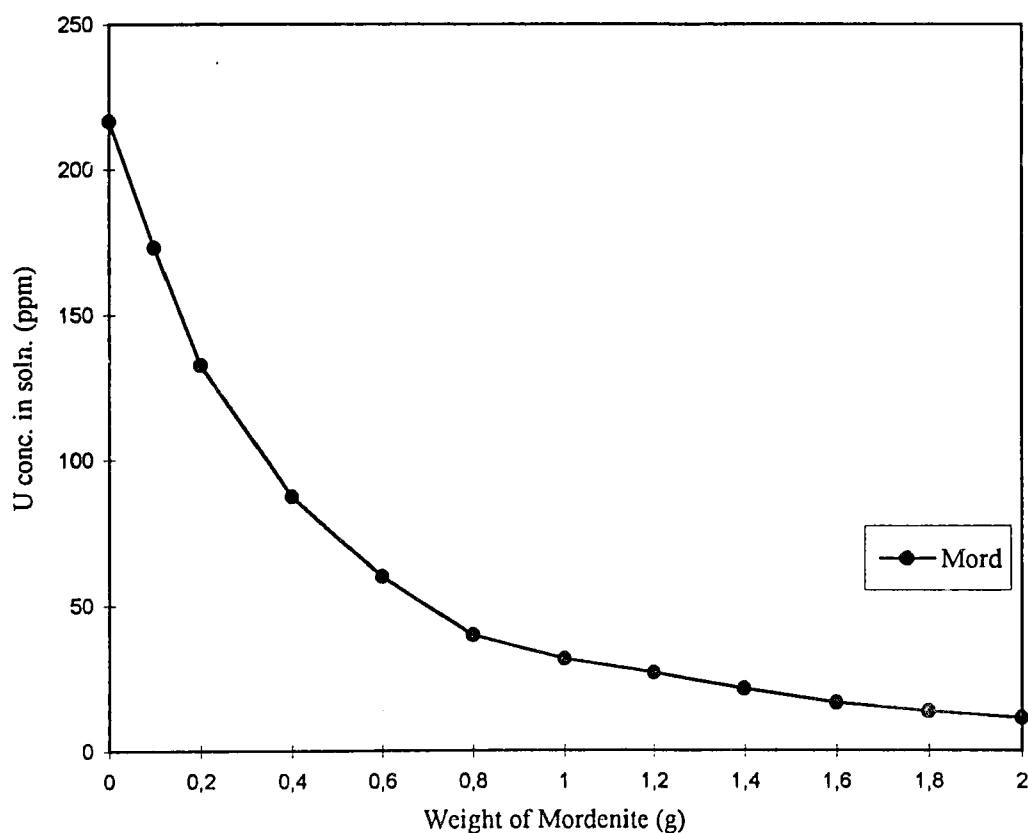
This study was performed under buffered conditions to determine which pH and what amount of mordenite shows the optimum conditions for uranium uptake. The equilibration time of 24 hours was utilized as previous results have shown that there is no significant uptake of uranium after 24 hours. In Figure 18, the pH 5.50 buffered system demonstrates the best uranium uptake while increasing in the amount of mordenite also increase uranium uptake, as expected.

Figure 18. Comparison of uranium uptake from 238 ppm U buffered solutions with increasing amount of mordenite.



In Figure 19, the pH 5.50 buffered system was also studied over the 0.1 to 2.0 g mordenite range. There is only a difference of 15 ppm between the 1.0 and the 2.0 g mordenite uranium uptake from a 238 ppm U solution. Therefore, the most cost effective optimum conditions for uranium removal from solution and potential for use in soil are pH 5.50 buffered, 1.0 g mordenite (per 20.0 ml solution of 238 ppm U), and 24 hours equilibrium time.

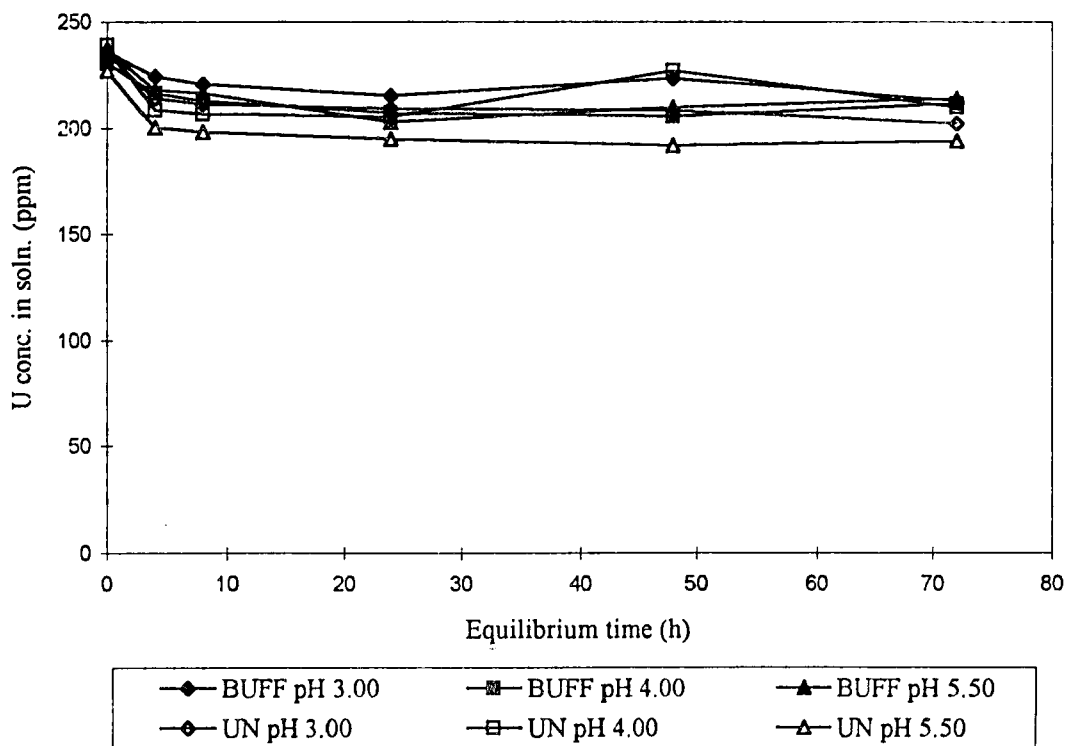
Figure 19. Uranium uptake from 238 ppm U pH 5.50 buffered solution with increasing amount of mordenite.



4.3.7 Comparison of Sodium vs. Calcium Exchanged Mordenite for Uranium Uptake

The mordenite-Ca form demonstrated poor uranium uptake at all pH's studied. Figure 20 show the best removal of uranium occurred in the pH 5.50 unbuffered system with a uranium uptake of 40 ppm from a 238 ppm U solution. The poor uptake can be attributed to the larger cation, Ca^{2+} , reducing the number of active sites in the mordenite framework than the sodium cation, Na^+ . The competition for these active sites can also be studied without exchanging the cation into the zeolite framework. The anionic framework of the zeolite has a certain number of active sites based upon the Si/Al ratio of the zeolite. Mordenite, a silica-rich type zeolite, typically has a Si/Al of approximately 9.5 to 11.²⁷

Figure 20. Uranium uptake from 238 ppm U buffered and unbuffered solutions with Mordenite-Ca form.



4.3.8 Uranium Uptake on Mordenite in the presence of Competing Cations

The optimum weight of 1.0 g mordenite was tested in the presence of known quantities of cations present in the soil as macronutrients. Figure 21A, shows the lower concentrations of competing cations were not disruptive to the uranium uptake by mordenite. On the contrary, in Figure 21B the mordenite uranium uptake was hindered by the presence of the larger quantities of cations. The Group II cations, Ca and Mg, had the most effect reducing the uptake by 20 and 25 percent, respectively. These results are similar to the findings of Qadeer et. al. Cations with larger charge to ionic radii ratio reduced the uptake of uranium on zeolite X.¹³ The potassium, a monovalent cation, had no adverse affect on the uptake of uranium by mordenite.

Figure 21A. Comparison of binary cation interferences for uranium uptake on mordenite from 238 ppm U buffered solutions at pH 5.50.

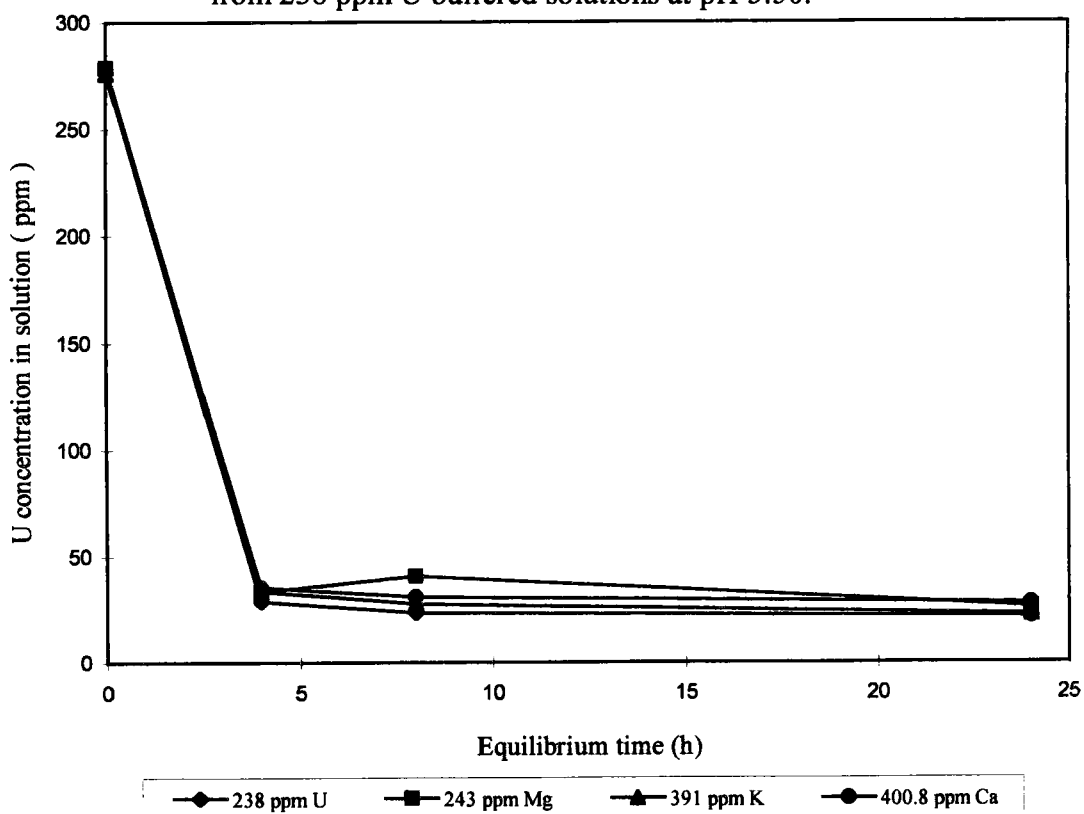
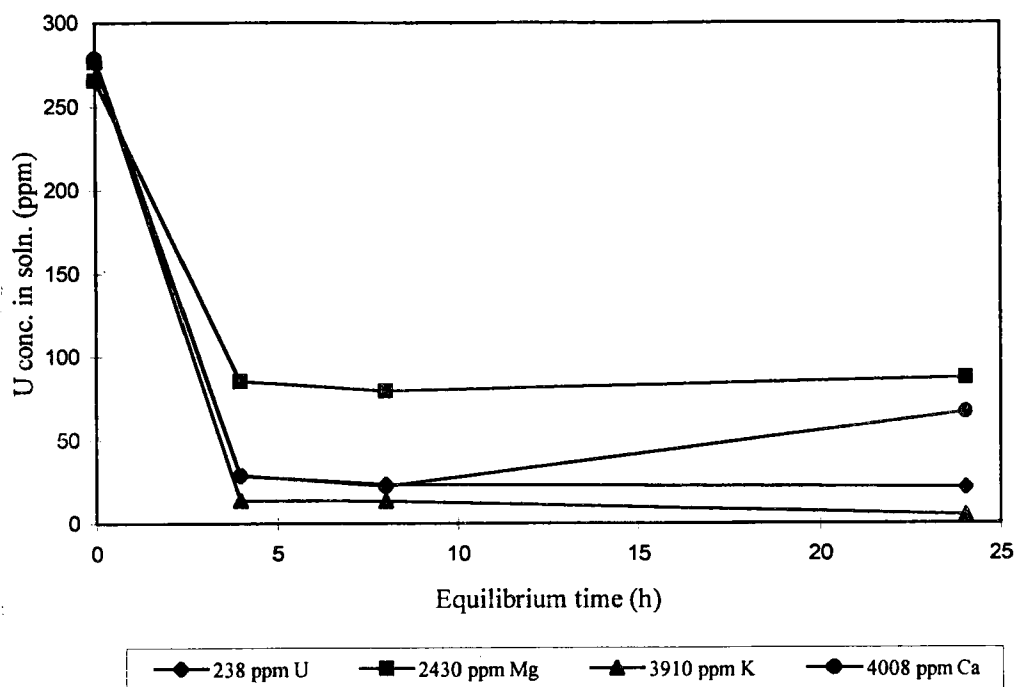


Figure 21B. Comparison of binary cation interferences for uranium uptake on mordenite from 238 ppm U buffered solutions at pH 5.50.



4.4 Desorption Studies

The desorption studies provided information on the kinetics of the release of uranium from sorbents. The results also showed a pH and time dependency.

4.4.1 Soil Desorption Study

After 72 hours, all of the samples examined had leached some of the uranium previously adsorbed by the soil. Preliminary batch studies involving the soil showed a maximum uptake of uranium from solution within 8 hours and a release of more than 50 percent of that adsorbed amount by the end of the batch study (72 hours). The highest leachate of uranium from the soil was observed in the pH 5.5 buffered 238 ppm U

solution which showed a release of 93 ppm U (35%) from the soil. These results indicate that the study of the ion exchange capabilities of soil must be performed before an uptake of uranium can efficiently take place as other cationic species work to decrease the uranium uptake.

4.4.2 Soil Desorption - Mordenite Adsorption Study

Results indicate that mordenite was able to adsorb most of the uranium leached from the soil and also aided in the release of more uranium from the soil. This higher release of uranium from the soil is only observed in the presence of the mordenite. The fine crystalline structure of mordenite may break down soil particles into smaller particles such that a release of more uranium from the soil occurs. The highest concentration of leachate uranium from the soil in the presence of mordenite was observed in the pH 5.5 buffered 238 ppm U solution which showed a release of 93 ppm U from the soil. Mordenite was found to remove at least 47 ppm (93 ppm - 46 ppm) of the uranium leachate from solution for the 238 ppm U system. This increased leaching effect of uranium from soil in the presence of mordenite should not occur in the actual contaminated site because there will not be any constant mixing of soil and mordenite in a reaction vessel.

4.4.3 Mordenite Desorption Studies

The use of double deionized water in an attempt to leach uranium that was previously adsorbed into the zeolite framework was found to be non-effective. The mordenite was found to leach less than 1 ppb U from its framework. Further desorption

tests were performed utilizing the same buffered and unbuffered systems as the process of uranium adsorption. These results showed that the stable microporous aluminosilicate framework of the mordenite is quite stable and the leaching of uranium was found not to occur in any significant levels.

4.5 Zeolite Composition Analysis

All zeolites were characterized by x-ray diffraction for phase purity and crystallinity. The samples were scanned from 5 to 50 2θ for one hour. A secondary confirmation was provided by FT-IR spectroscopy. The x-ray diffraction patterns for mordenite are shown in Figure 22. The peaks observed for mordenite are consistent with the major peaks of the sodium form of mordenite, Figure 23.²⁵ The confirmation is provided by the 2θ values of major peaks at 9.77, 21.45, 25.63, 26.04, 27.68, and 35.61.

The IR spectra for mordenite yielded three major peaks that confirm the framework of the zeolite. In Figure 24, the peak at 680-810 cm^{-1} shows the stretching of the Si-O lattice, a peak at 1080 cm^{-1} shows the antisymmetric stretching within the Si-O, and the peak at 1226 shows the external vibrations of the Si/Al-O₄.²⁷ The intensity of these peaks match well with the IR spectra of sodium form mordenite.

4.5.1 Calcium Analysis of Mordenite

Mordenite-Ca form samples digested in 1.0% HF were determined using ICP/MS to contain 140 ppm Ca indicating that the ion exchange of calcium into the zeolite framework for sodium occurred. The inclusion of calcium into the mordenite framework reduced the adsorption of uranium significantly, in all cases.

Figure 22. X-ray diffraction spectra of mordenite.

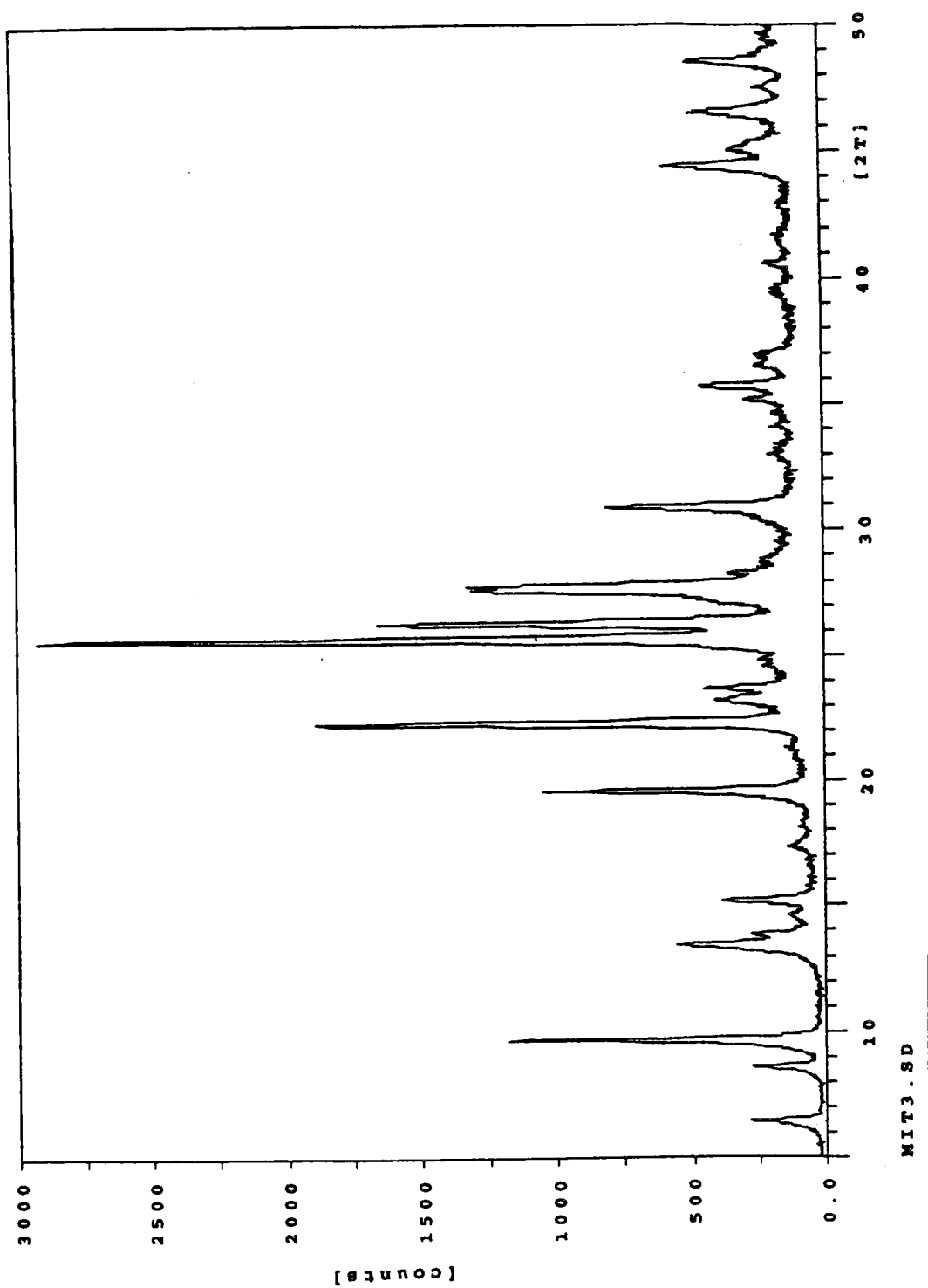


Figure 23. X-ray diffraction reference spectra of mordenite sodium form.²⁵

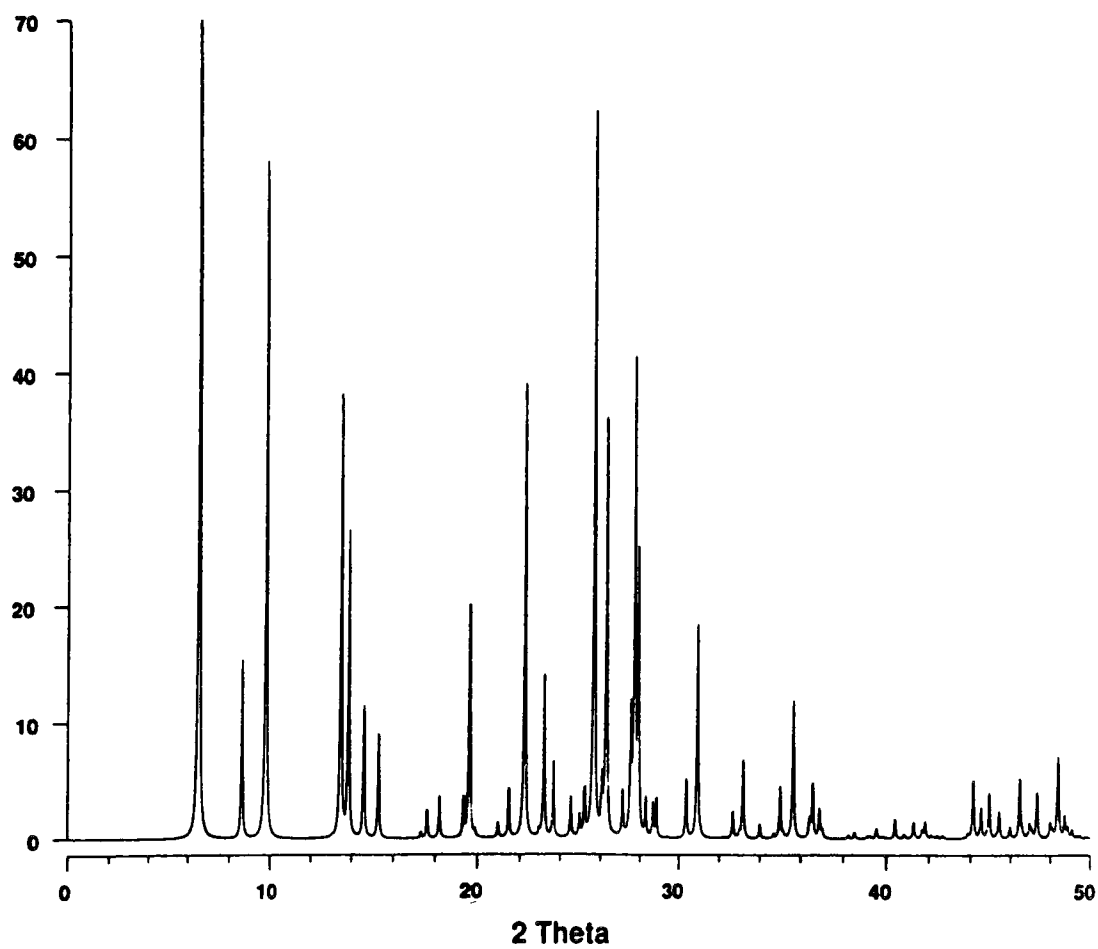
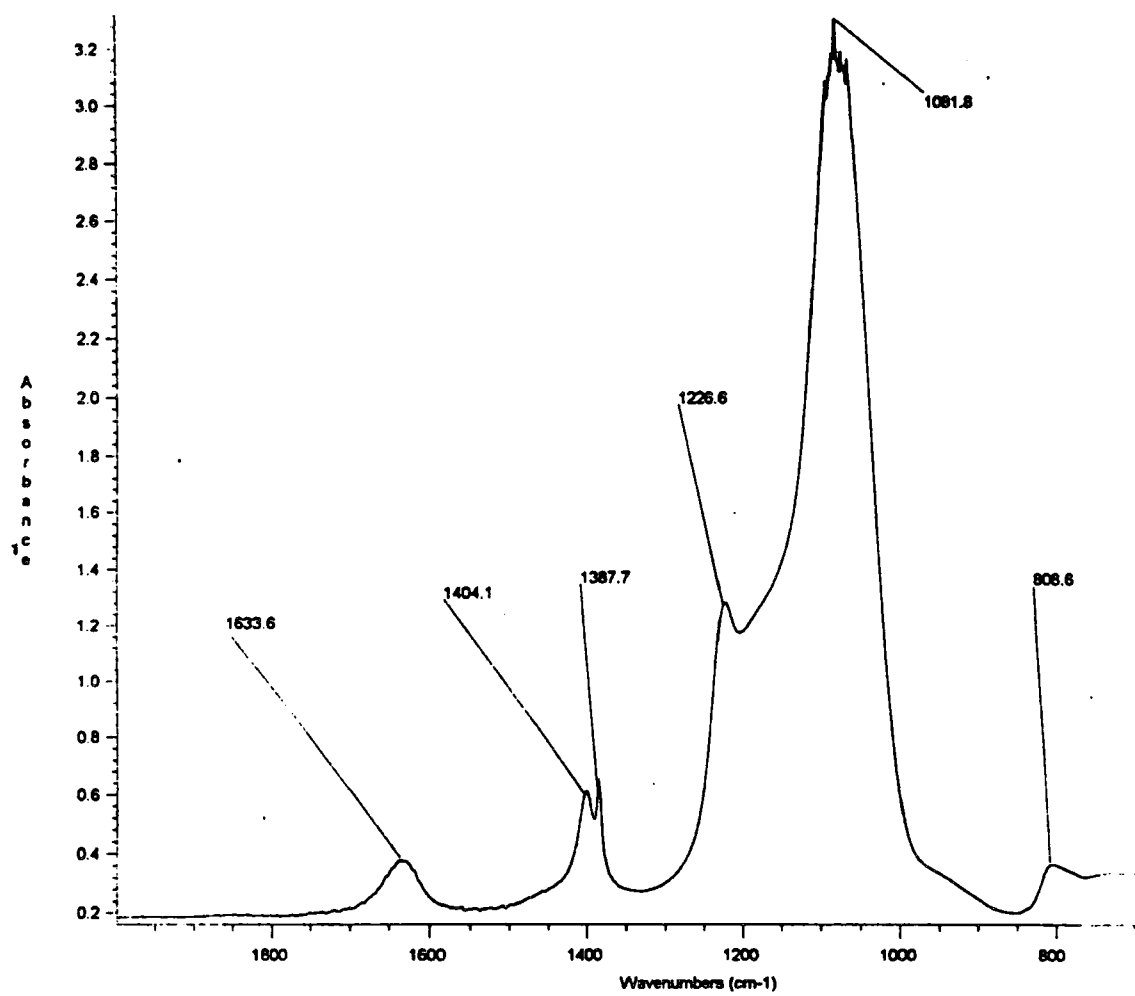


Figure 24. FT-IR spectra of mordenite.



4.5.2 Uranium Adsorption Analysis of Mordenite

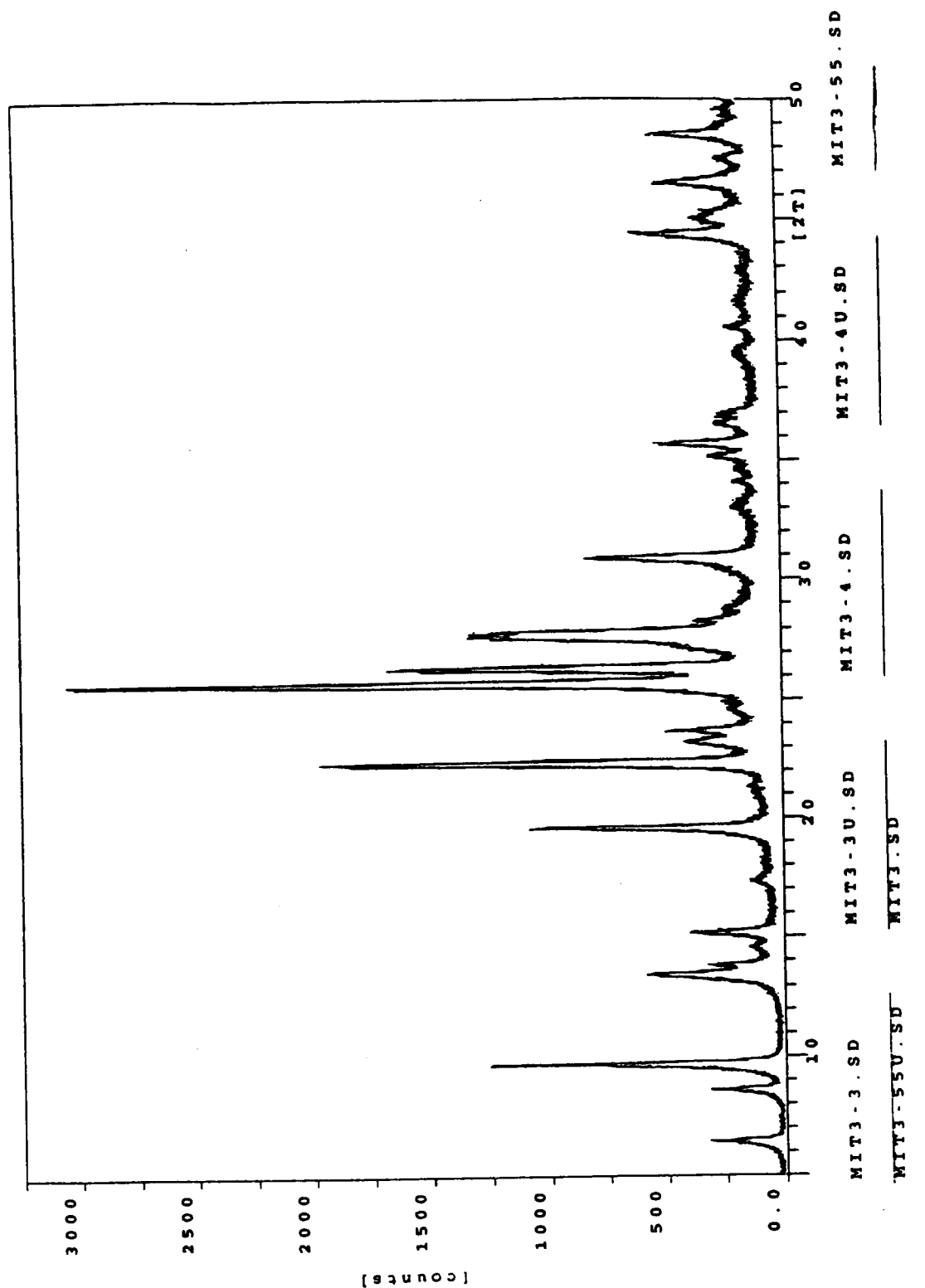
The samples that were digested were both from a batch study of 238 ppm U pH 5.50 buffered solution. The digested mordenite samples, #1 and #2, had previously adsorbed 102 and 84 ppm of uranium, respectively. Sample #1 contained 98.9 ppm U and sample #2 had 80.1 ppm U for a 97% uranium concentration accuracy of both samples. The process could not be via precipitation because the mordenite desorption studies revealed no presence of uranium in solution for mordenite samples that had removed uranium from solution. This result supports that the uranium is adsorbed by the mordenite.

4.6 Zeolite Stability Tests

The stability of the zeolite was measured by a comparison of the x-ray diffraction patterns of the original sample compared to that of the zeolite samples treated in the different pH solutions. Spectra of the treated mordenite was found to be consistent with the spectra of the original mordenite sample (Figure 25) suggesting no change in the framework of mordenite.

The ICP/MS data shows that the mordenite framework was not affected by the pH conditions of both the buffered and unbuffered systems. The mordenite was found to not leach any aluminum from its framework. These results supports the framework stability of the mordenite for these type of normal soil conditions.

Figure 25. X-ray diffraction spectra of treated mordenite vs. mordenite.



CHAPTER 5

SUMMARY AND CONCLUSIONS

Zeolites, having stable microporous alumino-silicate frameworks, have the capacity to exchange up to 2.2 mmol cations per gram of zeolite.¹⁶ Several zeolites have demonstrated the ability to remove uranium from solution. Uranium uptake was found to be dependent on solution pH, amount of sorbent, and cation concentration. The pH was determined to be a major contributing factor in uranium uptake based upon its affect on both the soluble UO_2^{2+} and the zeolite. The choice of buffer system utilized in the control of pH has also been shown to be a major factor. The formation of large uranium complexes with the ionic species of the buffer inhibit the ability of the zeolites to effectively ion exchange the uranium from solution.

Mordenite demonstrated significant uptake for uranium from solution with a maximum uptake of 93 percent in a pH 5.5 sodium acetate/acetic acid buffer system having a 23.8 ppm uranium concentration. Mordenite demonstrated superior performance to soil with a 85.5% uptake compared to only 46 % by the soil for a 238 ppm uranium solution . The uranium uptake on mordenite was slightly decreased in the presence of the soil. For a 1:1 ratio of soil to mordenite at optimum conditions of 238 ppm U and pH 5.50, mordenite showed a 52.5% uptake of uranium in the presence of the soil.

Mordenite, as with most zeolites, has a very stable framework composition such that the aluminum within its framework will not be leached out into the soil system to create further problems with the contaminated soil. Therefore, in a pH controlled

environment, mordenite has the ability to effectively suppress transport of residual uranium species and maintain the overall integrity of the soil system. In essence, mordenite is effective in the uptake of uranium for low concentrations at a pH of 5.50 where the uranium species are fairly soluble.

APPENDIX A

MATERIALS

Zeolites

Clinoptilolite (Ash Meadows, USA)
K-L (Chemie Uetikon EXAR 907)
Mordenite (Molecular Sieve Products #134907-4)
Y (Union Carbide #2218-10)
Zeolite X (Union Carbide #209)

Reagents

Acetic Acid (Fisher Scientific #A38c)
Ammonium Acetate (Fisher Scientific #A639-500)
Ammonium Chloride (Fisher Scientific #A661-500)
Ammonium Hydroxide (Fisher Scientific #A512-500)
Boric Acid (Fisher Scientific #A73-1)
Bromocrescol green-methyl red indicator (Fisher Scientific #LC11870-7)
Citric Acid (Fisher Scientific #A940)
Double Distilled Water (18.2 MΩ)
Glass Wool (Fisher Scientific #G12-145)
Isopropyl Alcohol, 99% (Fisher Scientific #A407-500)
Nitric Acid (HNO₃) ACS Plus Grade (Fisher Scientific #A200)
Potassium Bromide (Fisher Scientific #P227-25)
Sand (Fisher Scientific #S-06-03)
Silver Nitrate (Fisher Scientific #S181-500)
Sodium Acetate (CH₃COONa) (Fisher Scientific #S209)
Sodium Chloride (Fisher Scientific #S271-500)
Sodium Citrate (Fisher Scientific #S279)
Sodium Hydroxide (Fisher Scientific #S318-500)
Sulfuric Acid (Fisher Scientific #A510-212)
Uranium free soil (2 km from the FEMP site)
Uranyl Acetate (Electron Microscopy Sciences #950724)

Supplies

10.0 ml Volumetric Flasks (Fisher Scientific #20-812D)
20.0 ml Polyethylene Vials (Fisher Scientific #03-337-2)
250 ml polyethylene vials (Fisher Scientific # 02-923D)
50.0 ml Burettes (Fisher Scientific 03-700-20C).
Centrifuge (IEC-HN-S11)
Hydraulic Press
Mortar and Pestle
pH Meter (Orion 420A)

Supplies (continued)

Reciprocating Shaker (Eberbach 6000)
Sieve System (Fisher Scientific #12-04-399)
Tube Rotator (Fisher Scientific # 13-688-1D)
Whatman 2 Filter Paper (Whatman No. 6)

Intstrumentation

ICP-MS Perkin Elmer ELAN 5000

Phillips' X'Pert X-ray Diffractometer

Scan Time:	1 hour
Scan Range:	5 to 50 2θ
Voltage:	40 mV
Current:	40 mA
Slit Widths:	0.2 nm
Lamp:	CuK α 1

Fourier-Transform FT-IR Impact 400D Spectrometer

Number of sample scans:	64
Number of background scans:	64
Resolution:	4.000
Sample gain:	4.0
Mirror velocity:	0.6329
Aperture:	1.00
Detector:	DTGS Kbr
Beamsplitter:	Kbr
Source:	IR

APPENDIX B

CATION-EXCHANGE CAPACITY BY AMMONIUM SATURATION

Displacement and Distillation of Adsorbed Ammonium Method:

REAGENTS

1. Sodium chloride, NaCl (acidified): Prepare a 10% aqueous solution of NaCl (ammonia-free), and acidify it with enough HCl to make the solution approximately 0.005N with respect to acidity.
2. Sodium hydroxide (NaOH), 1N.
3. Boric acid (H_3BO_3), 2% solution.
4. Standard sulfuric acid (H_2SO_4), 0.1N.
5. Bromocresol green-methyl red mixed indicator: Triturate 0.1g of bromocresol green with 2 ml of 0.1N NaOH in an agate mortar, and add 95% ethyl alcohol to obtain a total volume of 100 ml. Triturate 0.1g of methyl red with a few ml of 95% ethyl alcohol in an agate mortar. Add 3 ml of 0.1N NaOH, and dilute the solution to a volume of 100 ml with 95% ethyl alcohol. Mix 75 ml of the bromocresol green solution with 25 ml of the methyl red solution, and dilute the mixture to 200 ml with 95% ethyl alcohol.

PROCEDURE

1. Leach the ammonium-saturated soil with 10% acidified NaCl until 225 ml have passed through the sample. Add small portions at a time, allowing each portion to pass through the sample before adding the next portion.
2. Transfer the leachate quantitatively to an 800 ml Kjeldahl flask, add 25 ml of 1N NaOH, and distill 60 ml of the solution into 50 ml of 2% H_3BO_3 .
3. Add 10 drops of bromocresol green-methyl red mixed indicator, and titrate the boric acid solution with standard 0.1N H_2SO_4 . The color change is from bluish green through bluish purple to pink at the end point.
4. Run blanks on the reagents.
5. Correct the titration figure for the blanks, and calculate the milliequivalents of ammonium in 100g of soil.

CATION-EXCHANGE CAPACITY BY AMMONIUM SATURATION

Ammonium Saturation Method:

REAGENTS

1. Ammonium acetate (NH_4OAc), 1*N*: Dilute 114 ml of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 ml of concentrated ammonium hydroxide (NH_4OH), and add water to obtain a volume of about 1,980 ml. Check the pH of the resulting solution, add more NH_4OH as needed to obtain a reaction of pH 7, and dilute the solution to a volume of 2 liters with water.
2. Isopropyl alcohol, 99%.
3. Ammonium chloride (NH_4Cl), 1*N*, adjusted to pH 7.0 with NH_4OH .
4. Ammonium chloride (NH_4Cl), 0.25*N*, adjusted to pH 7.0 with NH_4OH .
5. Ammonium oxalate [$(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$], 10%.
6. Dilute ammonium hydroxide (NH_4OH): Add 1 volume of concentrated NH_4OH to an equal volume of water.
7. Silver nitrate (AgNO_3), 0.10*N*.

PROCEDURE

1. Place 10 g of 2-mm, air-dried soil in a 500-ml Erlenmeyer flask, and add 250ml of neutral, 1*N* NH_4OAc .
2. Use 25 g of soil if the exchange capacity is very low, e.g., 3 to 5 me per 100 g.
3. Shake the flask thoroughly, and allow it to stand overnight.
4. Filter the soil with light suction using a 55-mm Büchner funnel or Pyres Büchner funnel (Corning size No.40). Do not allow the soil to become dry and cracked.
5. Leach the soil with the neutral NH_4OAc reagent until no test for calcium can be obtained in the effluent solution. (For the calcium test, add a few drops of 1*N* NH_4Cl , 10% ammonium oxalate, and dilute NH_4OH to 10 ml of the leachate in a test tube, and heat the solution to near boiling point. The presence of calcium is indicated by a white precipitate or turbidity.)
6. Leach the soil four times with neutral 1*N* NH_4Cl and once with 0.25*N* NH_4Cl .
7. Wash out the electrolyte with 150 to 200 ml of 99% isopropyl alcohol. When the test for chloride in the leachate (use 0.10*N* AgNO_3) becomes negligible, allow the soil to drain thoroughly.
8. Determine the adsorbed NH_4Cl .

CALCIUM-EXCHANGED FORM OF MORDENITE

Preparation of 1.00 M $\text{Ca}(\text{NO}_3)_2$

1. Weigh 164.08 g of calcium nitrate on an analytical balance.
2. Transfer to a clean 1000.0 ml volumetric flask. Add double deionized water to the mark.
3. Add a magnetic stirring bar and stir on stirrer until the solute is completely dissolved.
4. Transfer to a clean, dry 1.0 L polyethylene reagent bottle.

Displacement of Sodium from Mordenite

1. Weigh 5.00 g of Mordenite on an analytical balance.
2. Place in a 500 ml round bottom boiling flask.
3. Add 250 ml of 1.0 M $\text{Ca}(\text{NO}_3)_2$ solution.
4. Assemble the boiling flask to a standard distillation setup. Add a magnetic stirrer to boiling flask and reflux for 2 hours at 60 °C with constant stirring.
5. Allow solid to settle. Carefully decant the liquid and add another 250 ml aliquot of 1.00 M $\text{Ca}(\text{NO}_3)_2$ solution and reflux for 2 hours at 60 °C with constant stirring.
6. Repeat step 5.
7. Filter zeolite with light suction using a 55-mm Büchner funnel. Wash with aliquots of 100 ml double deionized water until test for nitrates is blank (usually 2-3).
8. Remove filter from funnel and allow zeolite to air dry overnight.

STOCK SOLUTION PREPARATION PROCEDURE

0.001 M Uranyl Acetate - $\text{UO}_2(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$:

1. Accurately weigh 0.4242 g of Uranyl Acetate (Formula weight 424.19 g) in the analytical balance in a weigh boat.
2. Carefully transfer the solid to a clean 1000 ml volumetric flask. Use a wash bottle filled with double distilled water to transfer all of the solid from the weigh boat to the flask.
3. Add double distilled water and fill to the mark. Mix thoroughly. Use a magnetic stirring bar and stirrer if necessary to insure complete mixing and dissolution of the solid.
4. Transfer the solution to a clean appropriate stock solution storage bottle, i. e., some solutions require glass, amber glass, plastic, etc. containers.

SIEVING PROCEDURE

1. The following is a list of the sieve screen sizes used in this laboratory:

10
25
35
45
60
80
120

2. The mesh size for the particle is determined by the sieve screen size. The smaller the number of the sieve screen the larger the particle size and vice-versa. If a particle is passed through a top screen and is in the second chamber, then its particle size is in the range of the two screen sizes. For example:

Top screen	35
Second screen	45
Third screen	80
Fourth screen	120

The particle mesh sizes from the sieve system would be:

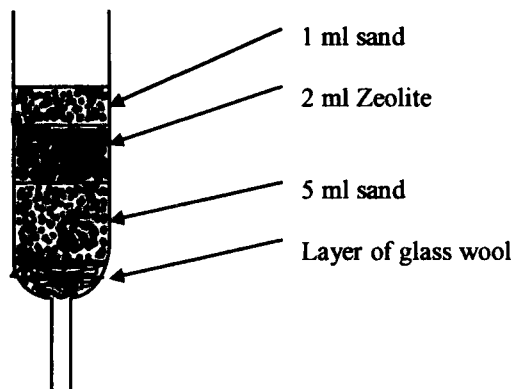
1) 35-45, 2) 45-80, 3) 80-120 and 4) 120+

3. Dry material in an oven at an appropriate temperature for the required time (if necessary).
4. Grind material in a mortar & pestle to a smaller particle size than original.
5. Select the desired mesh size for the material to be sieved.
6. Prepare the sieve chamber with the desired mesh screens in numerically ascending order (i.e., the smaller numbers on top and the larger numbers to the bottom).
7. Sieve the material to the desired mesh size (e.g., 35-45 or 45-80, etc.).
8. Place sieved material in properly labeled storage chambers or vials for future use.

COLUMN PACKING PROCEDURE

Percolated Method:

1. Clean columns should be packed with prepared materials only. Follow appropriate preparation techniques for the material that is to be used prior to packing the column, i. e., washing, drying, sieving, etc.
2. For a 10 ml bed volume, pack the column as follows:

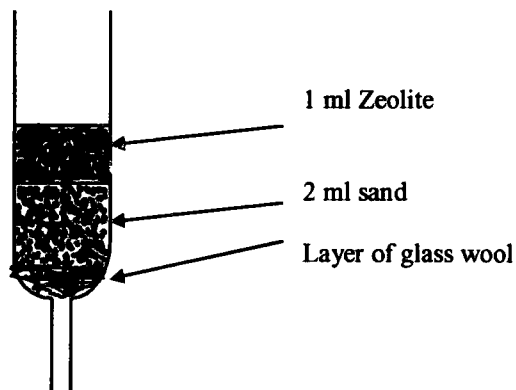


3. Make sure that the layers are level while packing. A solid glass rod can be used to pack the glass wool to the bottom of the column. Use care in not scraping the sides of the column with the glass wool, as it will scratch the column.
4. Rinse the packed column with aliquots of distilled water to insure complete packing of materials.

COLUMN PACKING PROCEDURE

Continuous Flow Method:

1. Clean columns should be packed with prepared materials only. Follow appropriate preparation techniques for the material that is to be used prior to packing the column, i. e., washing, drying, sieving, etc.
2. For a 3 ml bed volume, pack the column as follows:



3. Make sure that the layers are level while packing. A solid glass rod can be used to pack the glass wool to the bottom of the column. Use care in not scraping the sides of the column with the glass wool, as it will scratch the column.
4. Rinse the packed column with aliquots of distilled water to insure complete packing of materials.

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